



INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION



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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

SCANNING TUNNELING MICROSCOPY

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These are preliminary lecture notes, intended only for distribution to participants.

1988 ICTP Spring College in Condensed Matter Physics

Scanning Tunneling Microscopy

R. M. Feenstra

IBM Yorktown Heights

1. Historical Review

2. Apparatus

3. Microscopy

(a) image interpretation (metal vs. semiconductors)

(b) surface buckling - GaAs(110)

(c) surface reconstruction - Si(111)2x1

4. Spectroscopy

(a) tunneling theory

(b) ordered surface states - Si(111)2x1

(c) semiconductor effects - GaAs(110)

(d) charge of adsorbates - O/GaAs(110)

(e) disordered surface states - Sb/GaAs(110)

5. Other Applications/Techniques

Pre-STM Related Work (partial list):

A. Solid Barrier Tunneling:

1. L. Esaki, "New phenomena in narrow Germanium p-n junctions", Phys. Rev. **109**, 603 (1958).

2. I. Giaver, "Energy gap in superconductors measured by electron tunneling", Phys. Rev. Lett. **5**, 147 (1960).

3. R. C. Jaklevic and J. Lambe, "Molecular Vibration Spectra by Electron Tunneling", Phys. Rev. Lett. **17**, 1139 (1966).

B. Squeeze Tunneling:

1. J. Moreland and P. K. Hansma, "Electromagnetic squeezer for compressing squeezable electron tunneling junction", Rev. Sci. Instr. **55**, 399 (1984).

C. Measurement of Surface Forces:

1. J. N. Israelachvili and D. Tabor, "The measurement of van der Waals dispersion forces in the range 1.5 to 130 nm", Proc. Roy. Soc. A**331**, 19 (1972).

D. Vacuum Tunneling:

1. R. Young, J. Ward, and F. Scire, "Observation of Metal-Vacuum-Metal Tunneling, Field Emission, and the Transition Regime, Phys. Rev. Lett. **27**, 922 (1971).
2. W. A. Thompson and S. F. Hanrahan, "Thermal drive apparatus for direct vacuum tunneling experiments ", Rev. Sci. Instr. **47**, 1303 (1976).
3. E. C. Teague, "Room-Temperature Gold-Vacuum-Gold Tunneling Experiments ", Bull. Amer. Phys. Soc. **23**, 290 (1978).

E. Fowler-Nordheim Tunneling & Scanning:

1. R. D. Young, "Surface Microtopography " Physics Today, **24**, 42 (1971).
1. R. D. Young, J. Ward, and F. Scire, "The Topografiner: An Instrument for Measuring Surface Microtopography ", Rev. Sci. Instr. **43**, 999 (1972).

Early Papers:

1. G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, "Tunneling through a controllable vacuum gap ", Appl. Phys. Lett. **40**, 179 (1982).
2. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, "Surface Studies by Scanning Tunneling Microscopy ", Phys. Rev. Lett. **49**, 57 (1982).
3. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, "7x7 Reconstruction on Si(111) Resolved in Real Space ", Phys. Rev. Lett. **50**, 120 (1983).

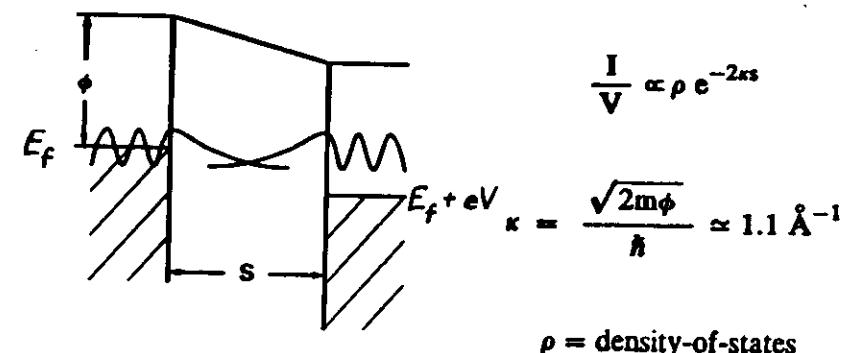
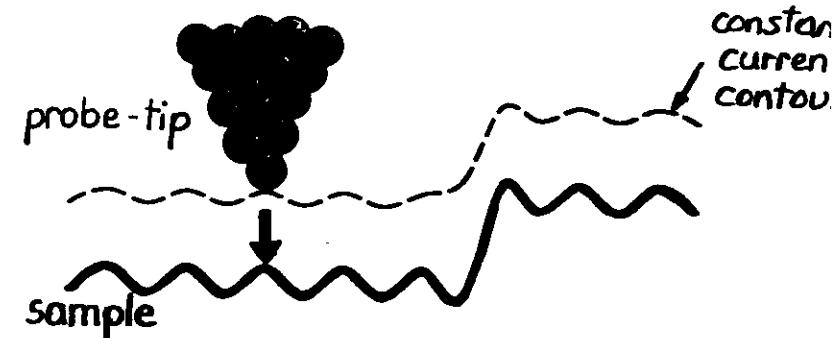
Reviews:

1. G. Binnig and H. Rohrer, Helv. Phys. Acta **55**, 726 (1982).
2. G. Binnig and H. Rohrer, Surf. Sci. **152/153**, 17 (1985).
3. G. Binnig and H. Rohrer, IBM J. Res. Devel. **30**, 355 (1986).
4. P. K. Hansma and J. Tersoff, J. Appl. Phys. **61**, R1 (1987).

Conference Proceedings:

1. IBM Journal of Research and Development, Vol. 30, No. 4 & 5 (1986).
2. Surface Science, Vol. 181, No. 1 & 2 (1987).
3. Journal of Vacuum Science and Technology A, March/April (1988).

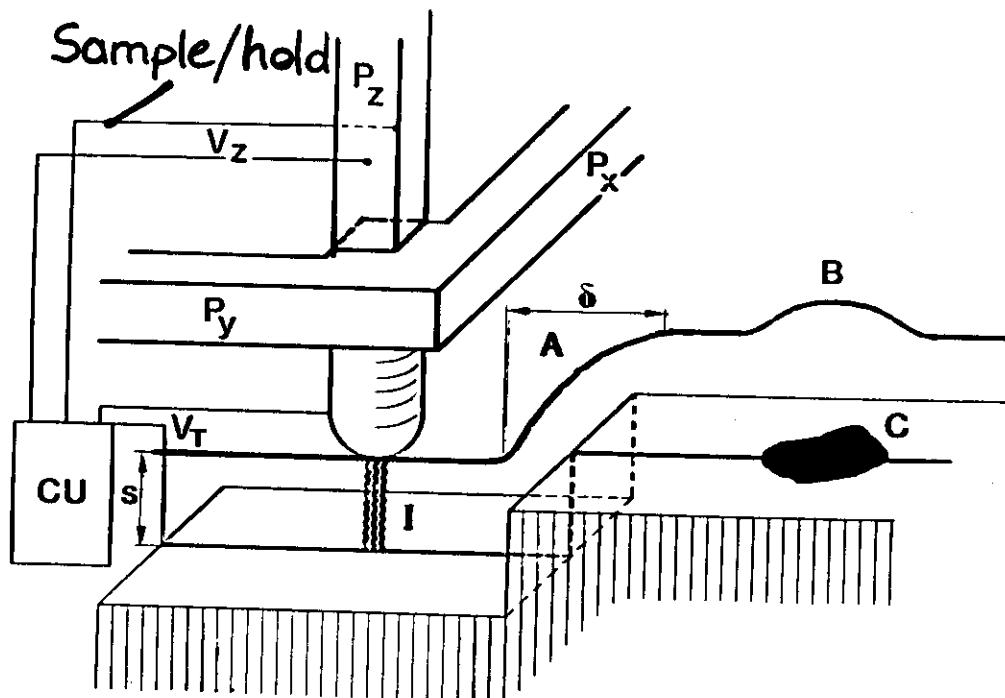
STM - G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel,
Phys. Rev. Lett. 49, 57 (1982).



(Tersoff + Hamann,
PRL 50, 1998 (1988))

STM

G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel,
Phys. Rev. Lett. 49, 57 (1982).



P_x , P_y , P_z - Piezo-electric elements

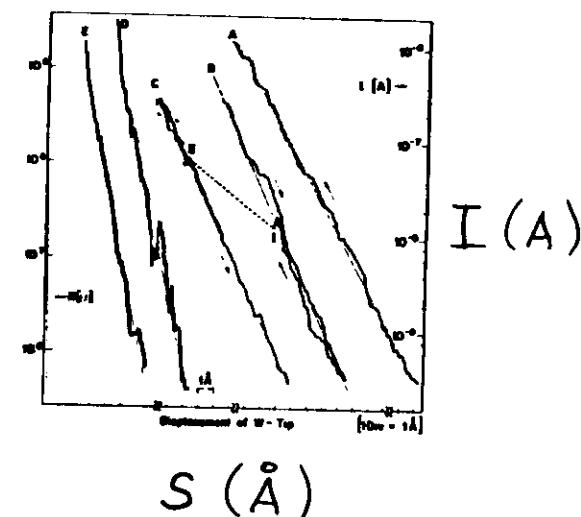
CU - Feedback control unit

Sample/hold - spectroscopic measurements

7

Exponential dependence of
tunneling current:

(Binnig, Rohrer, Gerber, Weibel, Appl. Phys. Lett.
40, 178 (1982))



previous work:

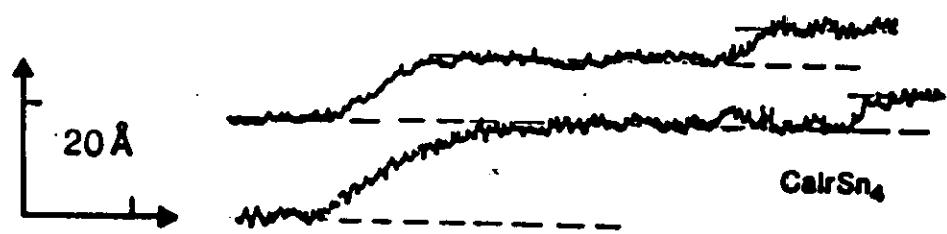
Young, Ward, Scire, Rev. Sci. Instr. 43, 999 (1972)
Thompson, Hanrahan, Rev. Sci. Instr. 47, 1303 (1976)

8

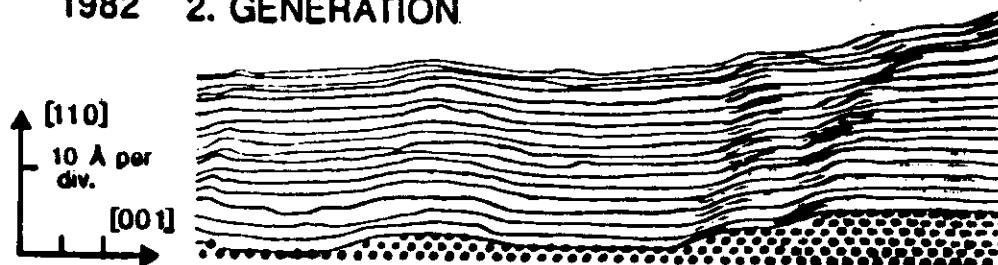
Binnig, Rohrer, Gerber, Weibel - IBM Zürich

EVOLUTION OF STM

1981 1. GENERATION



1982 2. GENERATION

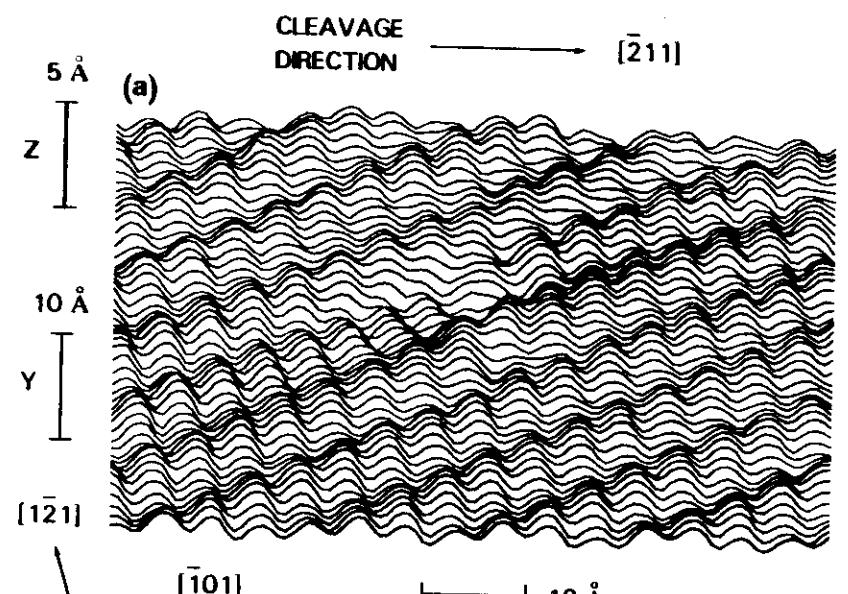


1983 3. GENERATION

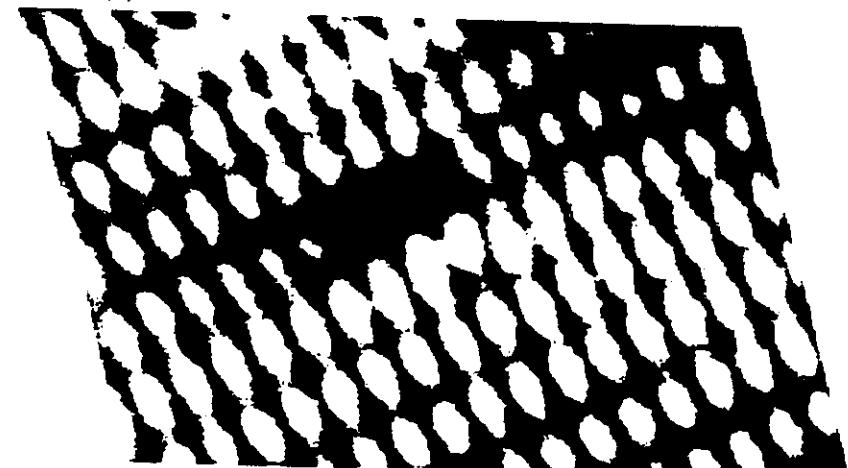


9

Si(III) 2×1

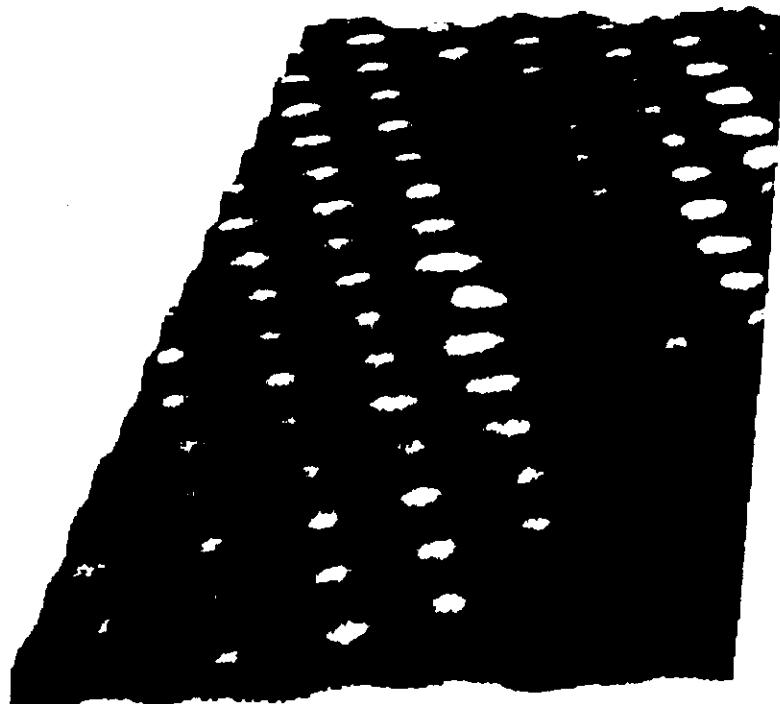


(b)



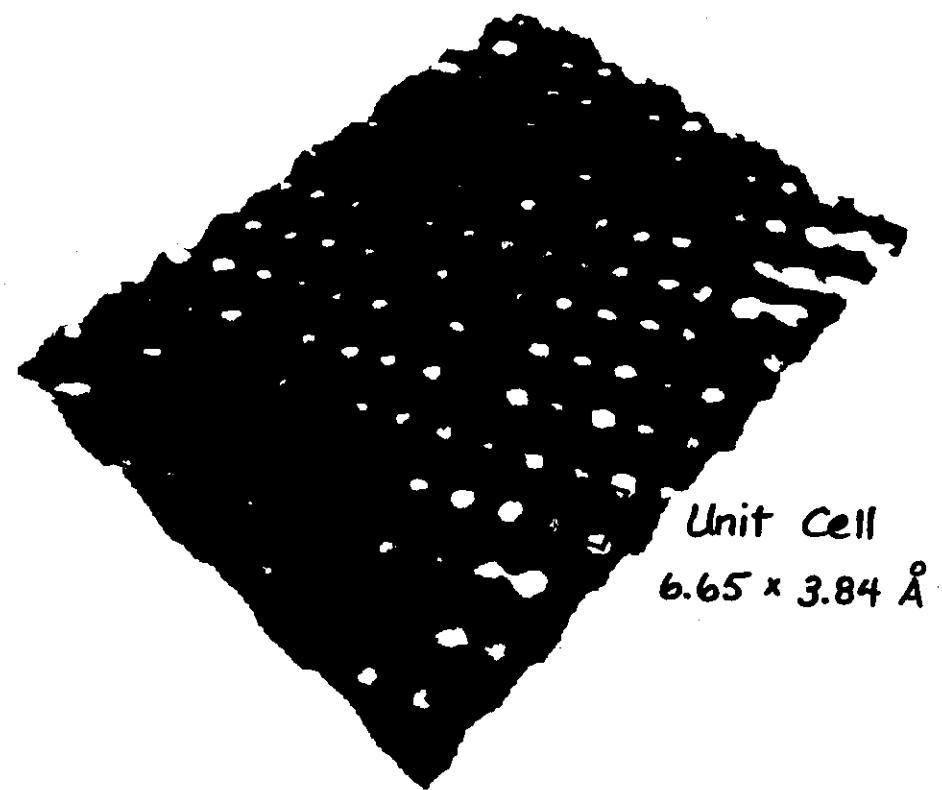
10

Si(m) 2x1



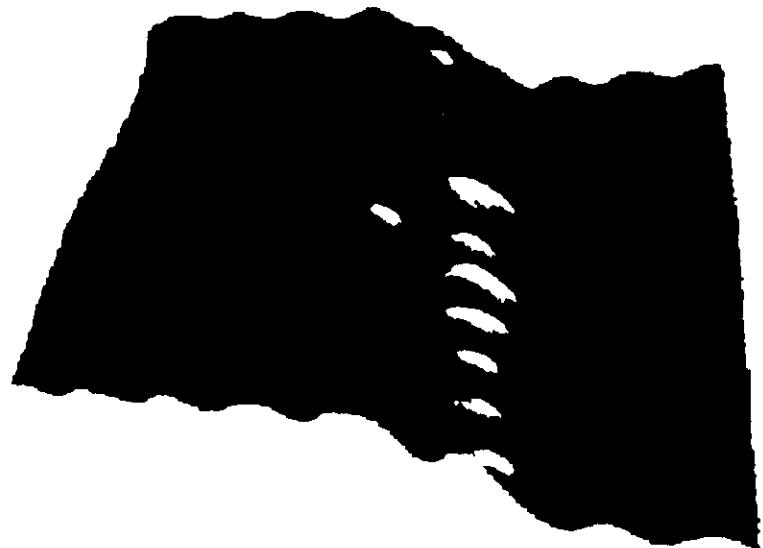
11

Si(m) 2x1



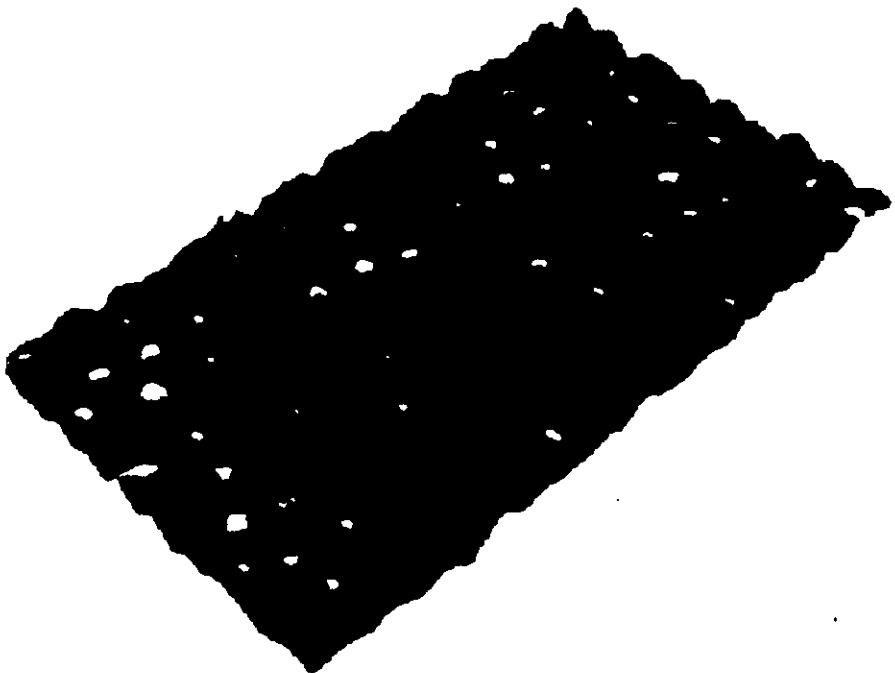
12

$\text{Si}(111) 2 \times 1$ mono-atomic step



13

$\text{Si}(111) 7 \times 7$



14

Components of STM: (Binnig, et. al.)

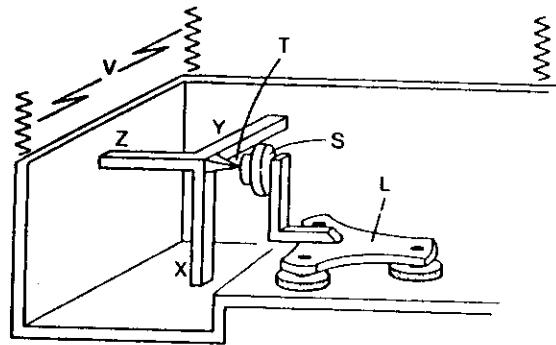
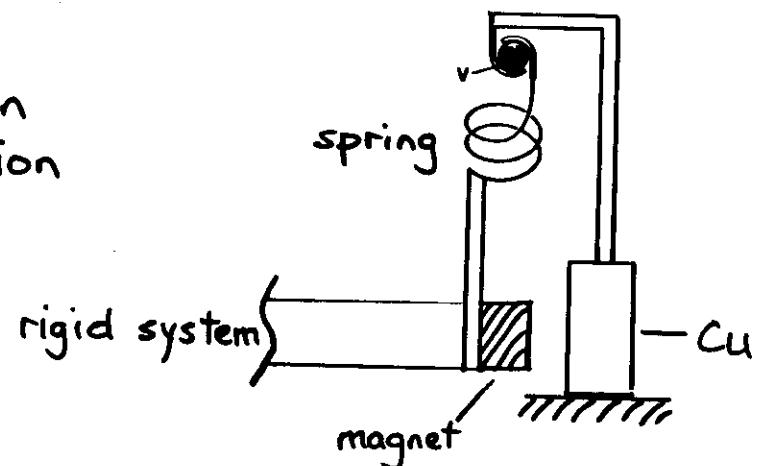
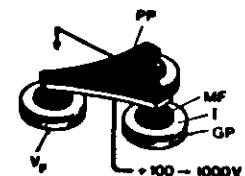


FIG. 1. Schematic of a STM using a piezotriod, ($X-Y-Z$) for fine positioning of the tunnel tip T and a piezomotor L for rough positioning of the sample S. Vibration isolation is achieved with coil spring V and eddy-current damping (not shown).

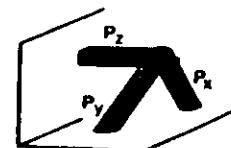
a) vibration isolation



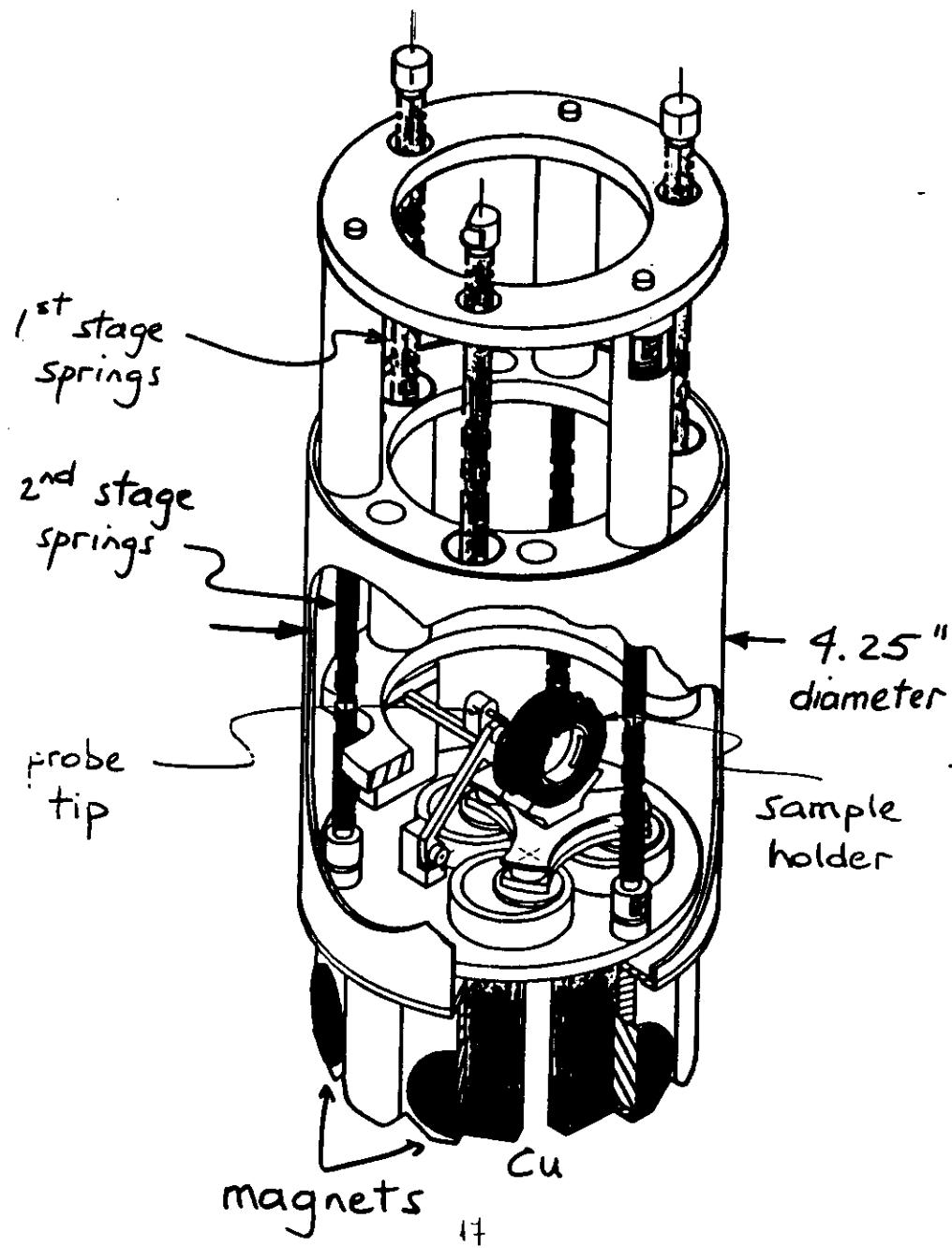
b) coarse motion "louise" ($1\text{ }\mu\text{m} - 1\text{ cm}$)



c) fine motion piezo-tripod ($0.1\text{ \AA} - 1\text{ }\mu\text{m}$)

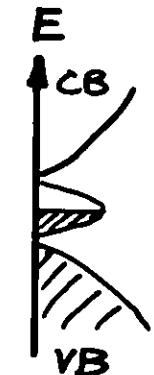
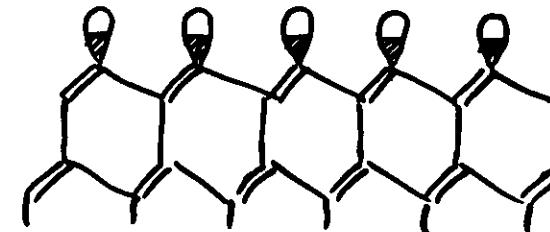


Ch. Gerber, G. Binnig, H. Fuchs, O. Marti, H. Rohrer,
Rev. Sci. Instr. 57, 221 (1986).



Surface Reconstructions:

(III)

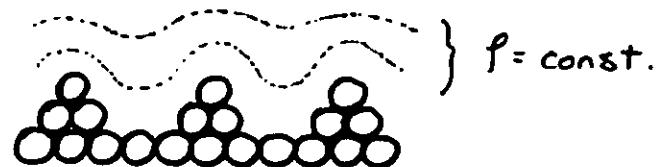


↳ buckling model

Where are the atoms ?
Where are the electrons ?

Interpretation of Images

Metals - state-density follows atoms



→ place ball of charge $f_i \sim e^{-\beta(r-R_i)}$ around each atom,

and sum $f_{tot} = \sum_i f_i$,

Search for contour of constant f .

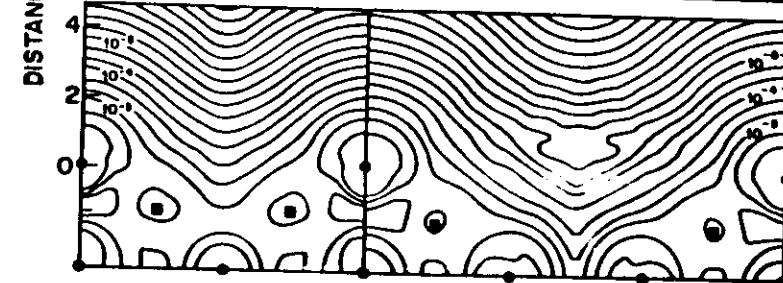
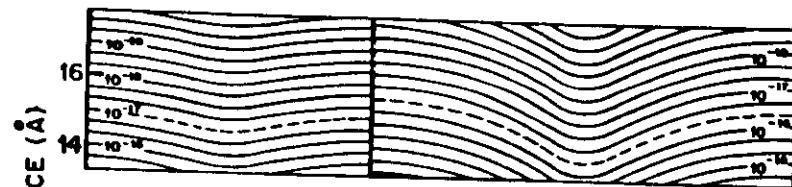
"CHARGE SUPERPOSITION"

Semiconductors -

state-density does not follow atoms

- Charge superposition usually not applicable, even to lowest order.
- Look at electronic band-structure.

J. Tersoff + D.R. Hamann, Phys. Rev. B 31, 805 (1985).



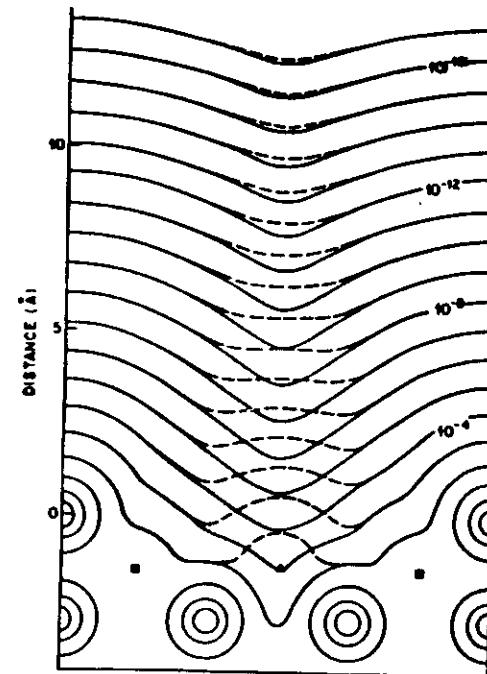
Au(110) 2x1, 3x1

$\delta(\vec{r}, E_f)$ by LAPW

- in-plane atom
- out-of-plane atom

Au (110) 2x1 →
charge-superposition

- atoms as shown
- extra atom ▲



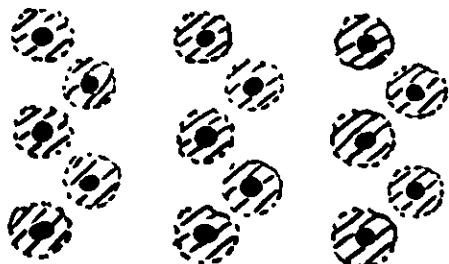
STM images of semiconductors:

tight-binding

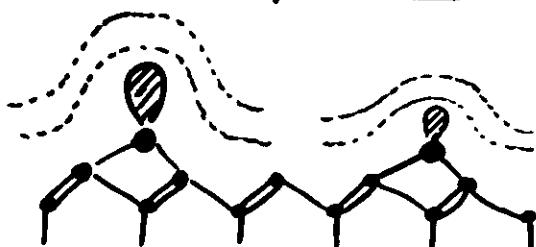
$$\psi_j \sim \sum_i a_{ij} \phi_i(r - R_i)$$

dangling bond on i^{th} atom

lateral position: (x, y)



vertical position: (z)



STM sees atoms with dangling bonds, but not all atoms are seen equally.

$$\Delta(x, y) \sim 1 \text{ \AA}$$

voltage-dependence

difficult to distinguish between atomic height and magnitude of state-density.

Δz large!

"normalization" of data

Tersoff and Hamann

LAPW expansion
thin-slab geometry

GaAs (110)

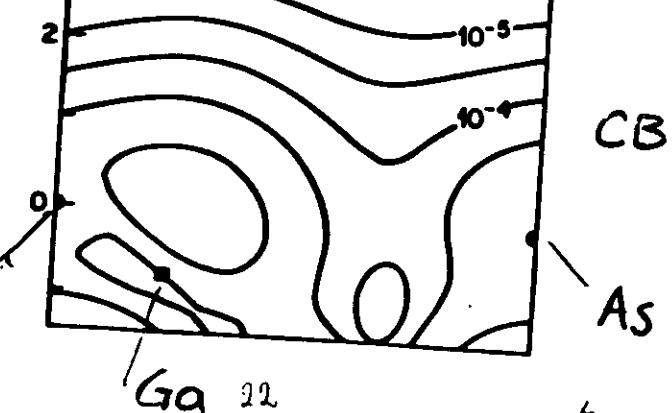
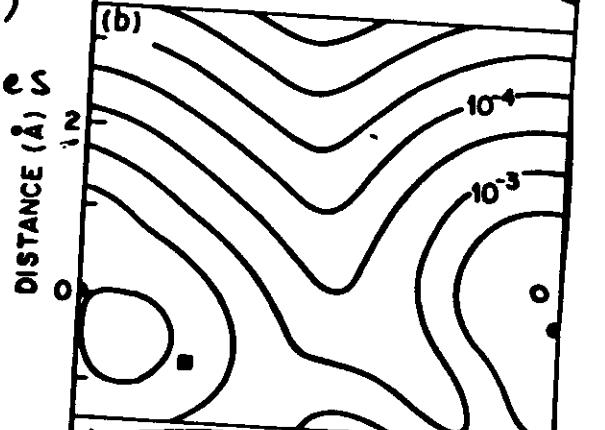
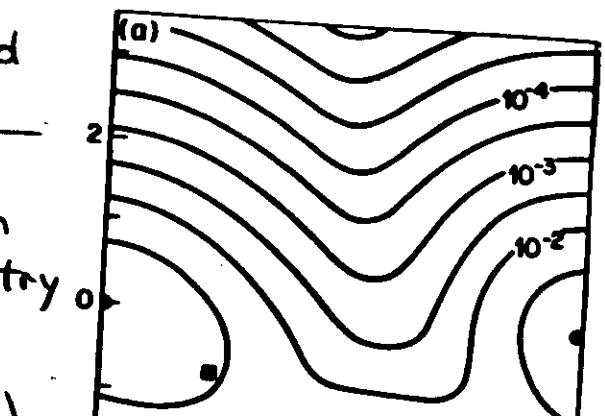
charge densities

(110)

(001)

As

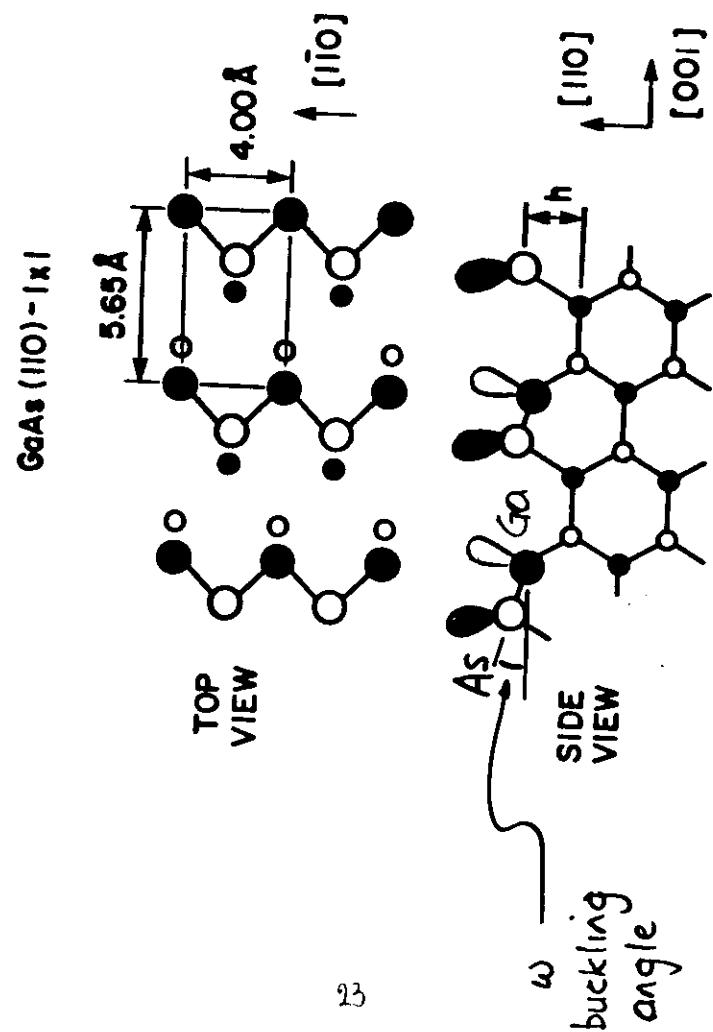
C + V



VB

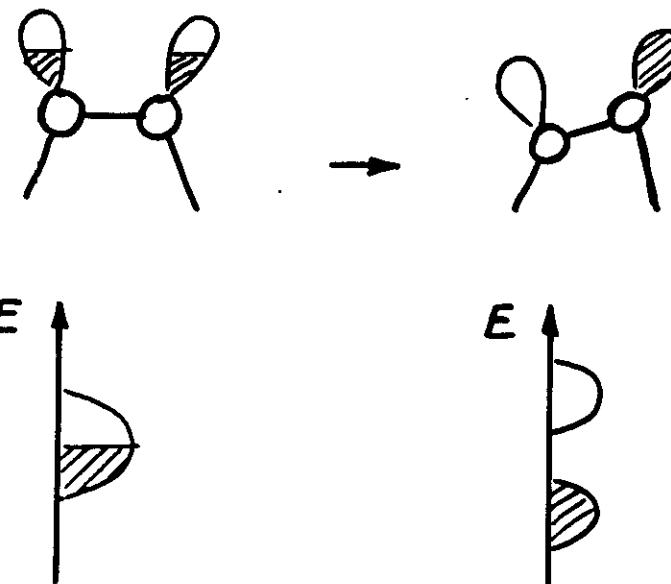
CB

As



23

Buckling: charge transfer between equivalent or inequivalent atoms

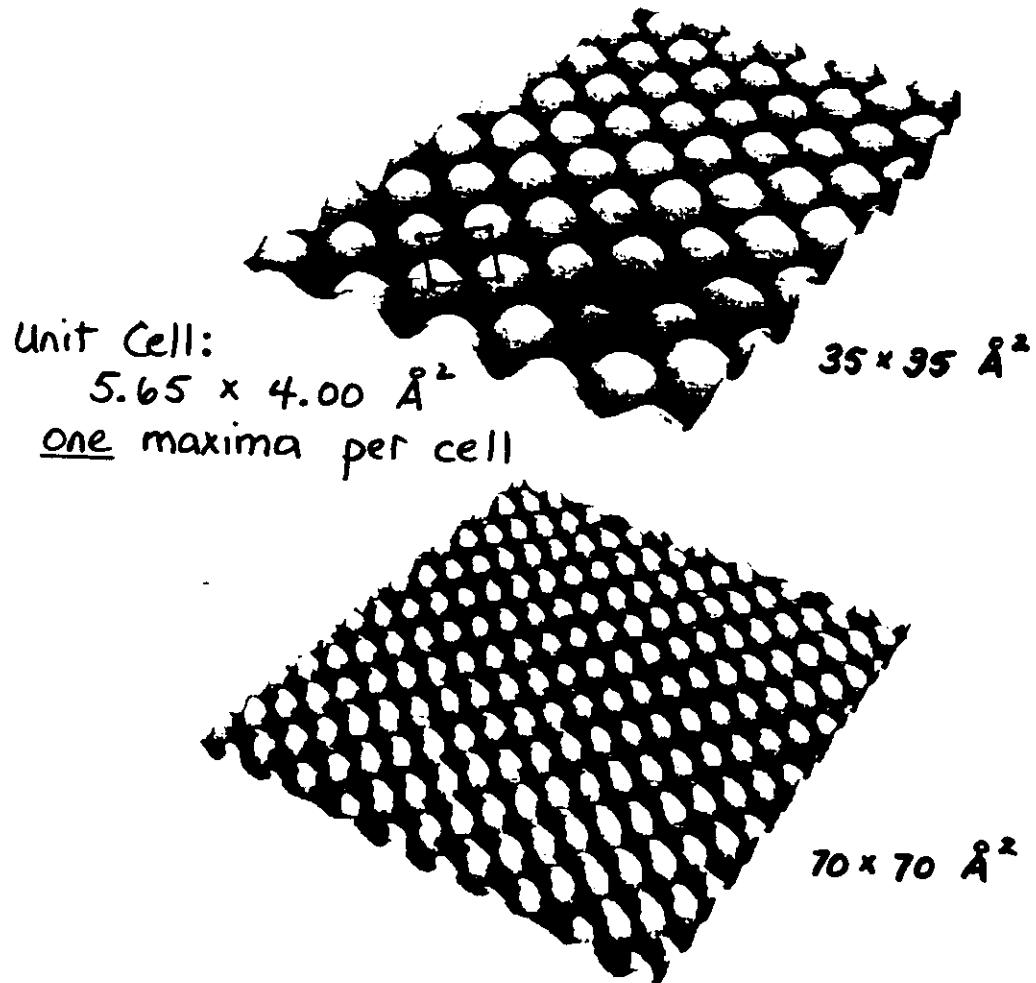


Energy is lowered.

Filled states on up atoms,
Empty states on down atoms.

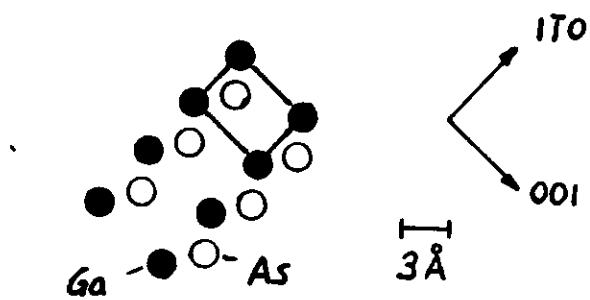
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GaAs (110) - 1x1



25

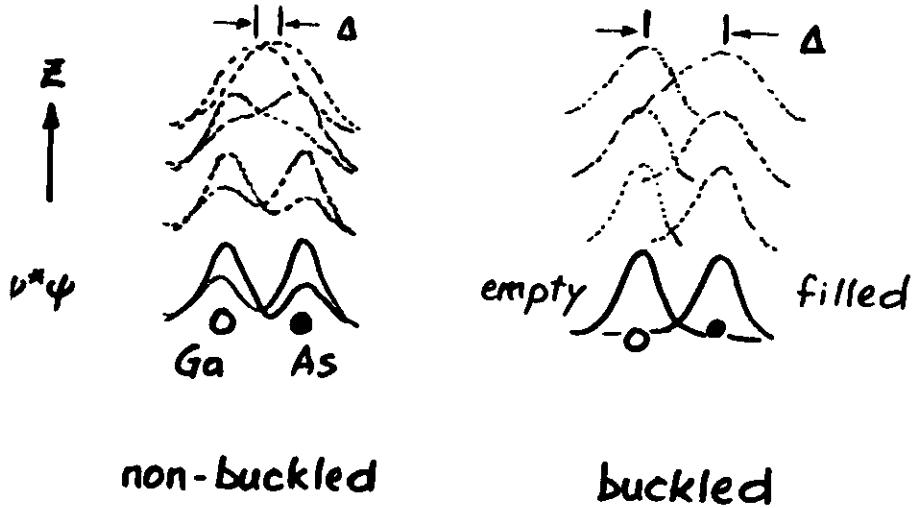
GaAs (110)



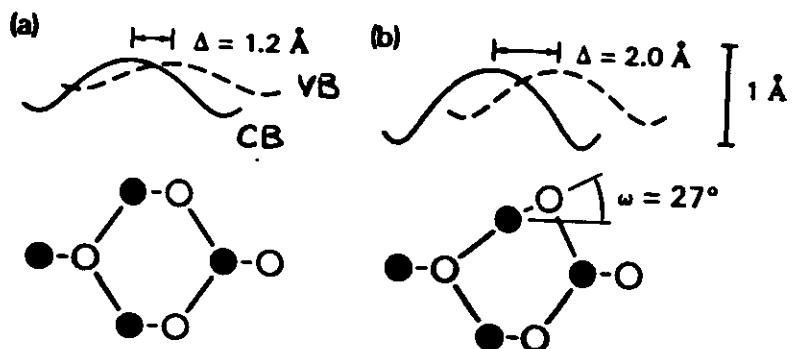
26

GaAs(110) - Structural Dependence of State - Density

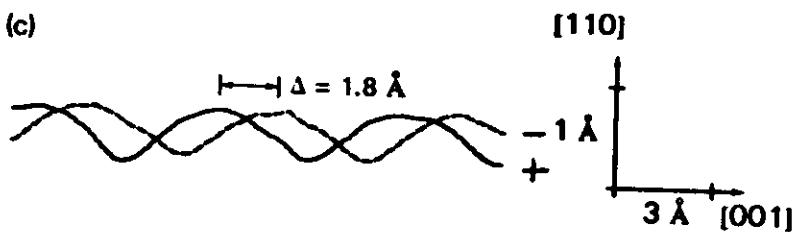
Lateral Shift between Empty and Filled States



THEORY:



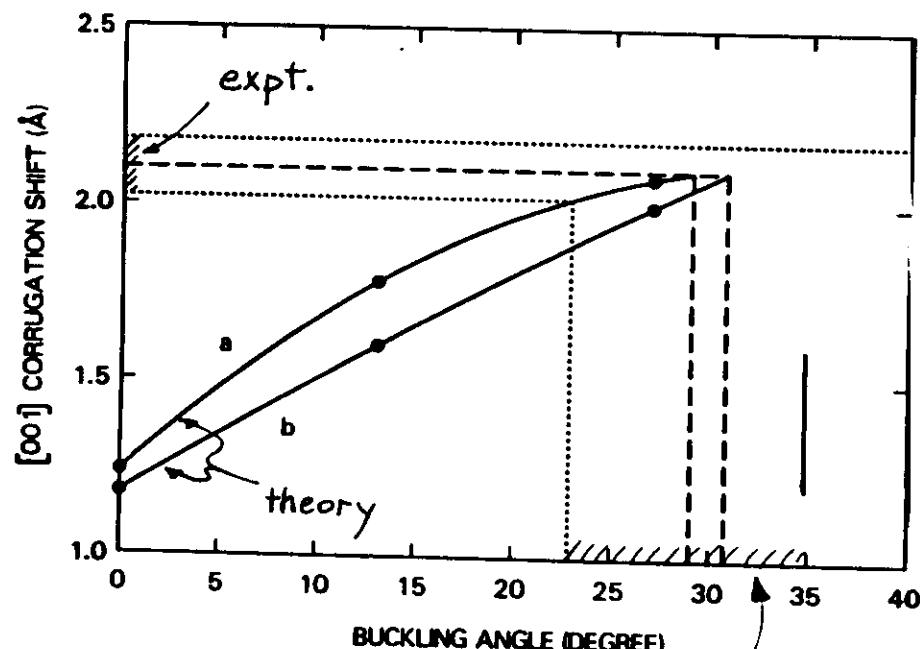
EXPERIMENT:



$$\bar{\Delta} = 2.10 \text{ \AA} , \quad \frac{\sigma}{N} = 0.08 \text{ \AA}$$

GaAs (110) images:

- chemical difference : large effect
Ga. vs. As
electronegativity
- determination of structural parameter
(buckling) : small effect

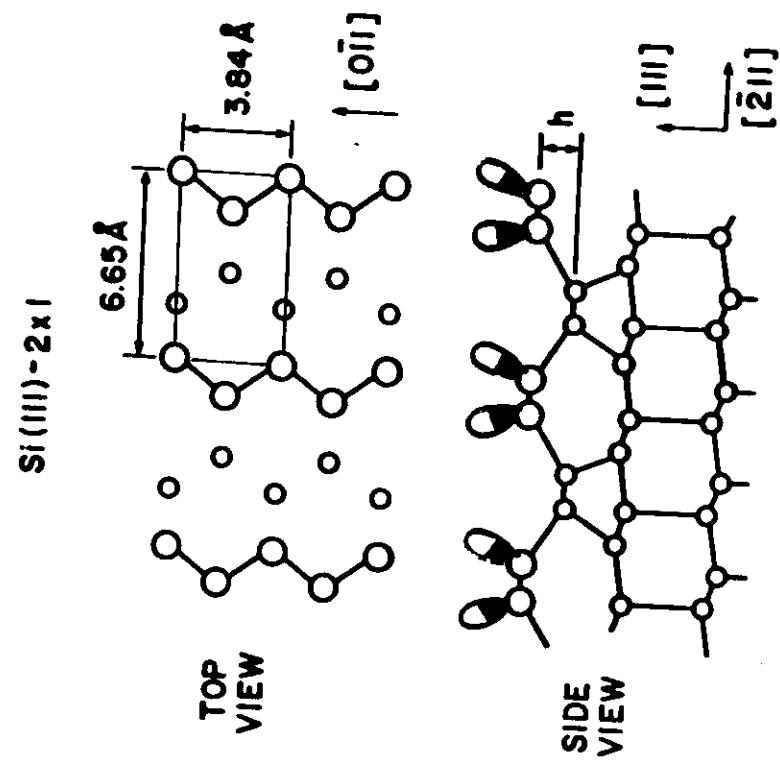


a) $s = 5.7 \text{ \AA}$

b) $s = 7.5 \text{ \AA}$

determined range of buckling

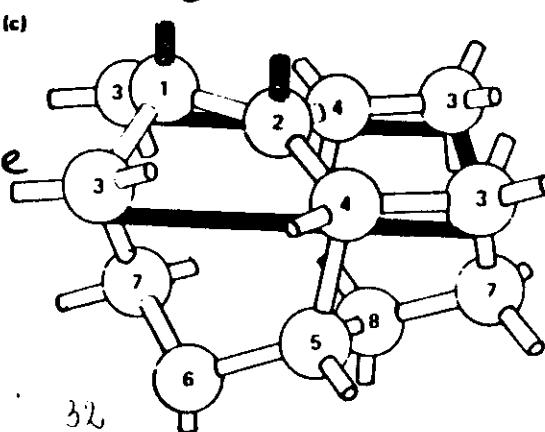
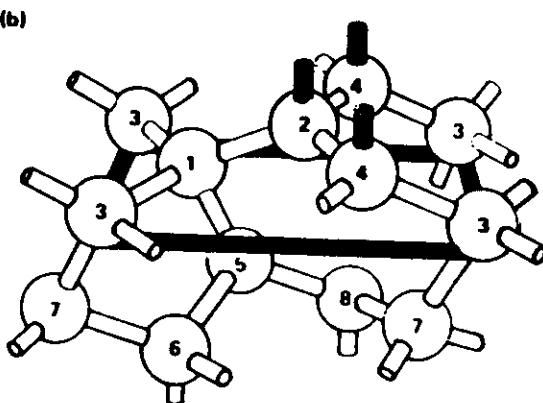
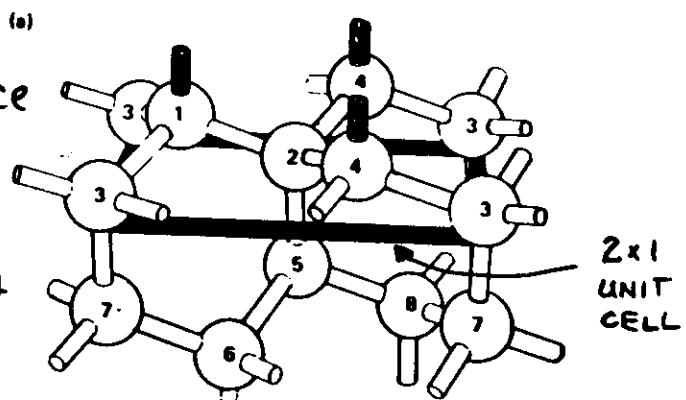
Figure from Nielsen, Martin, Chadi and Kunc,
JVST B1, 714 (1983) :



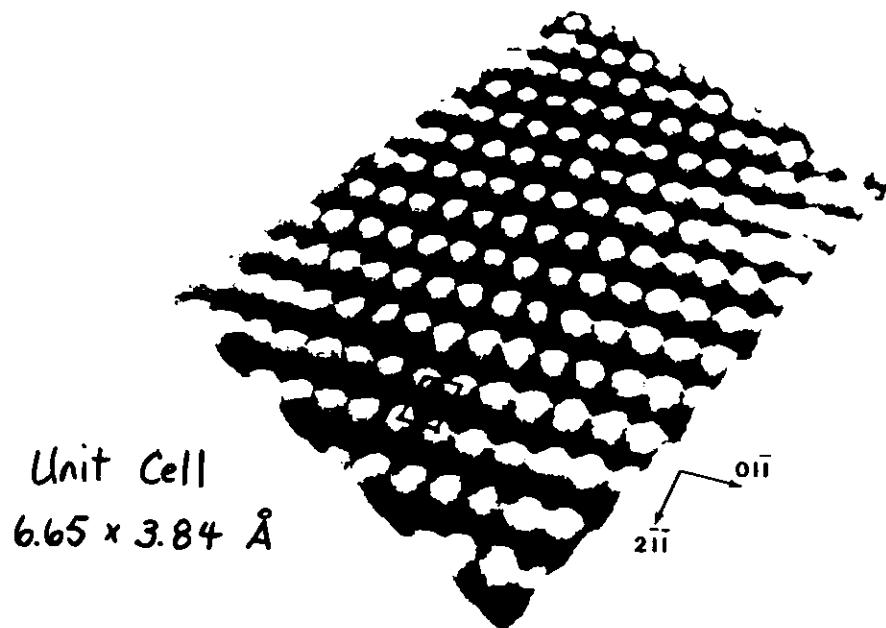
Buckled { lower 1
raise 4
Haneman (1961)

π -bonded chain
Pandey (1981)

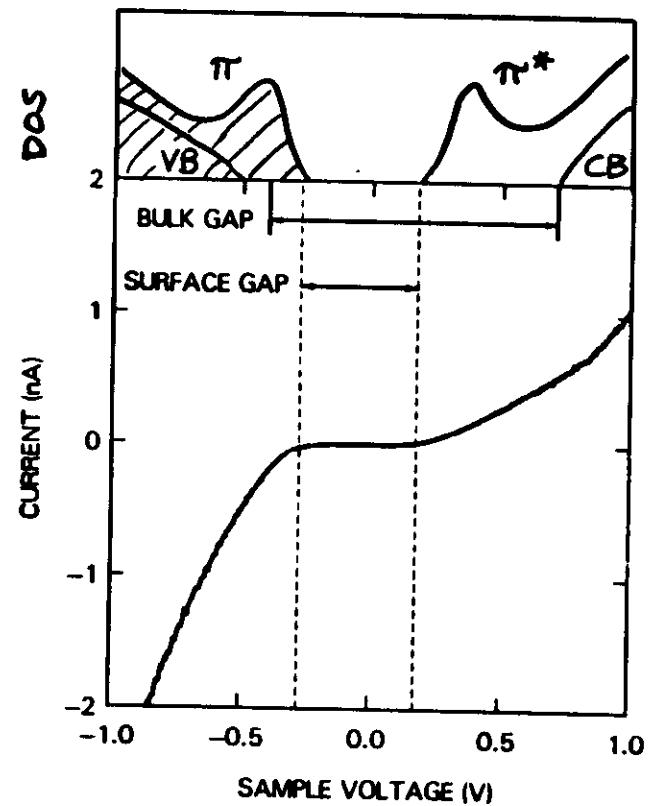
π -bonded molecule
Chadi (1982)

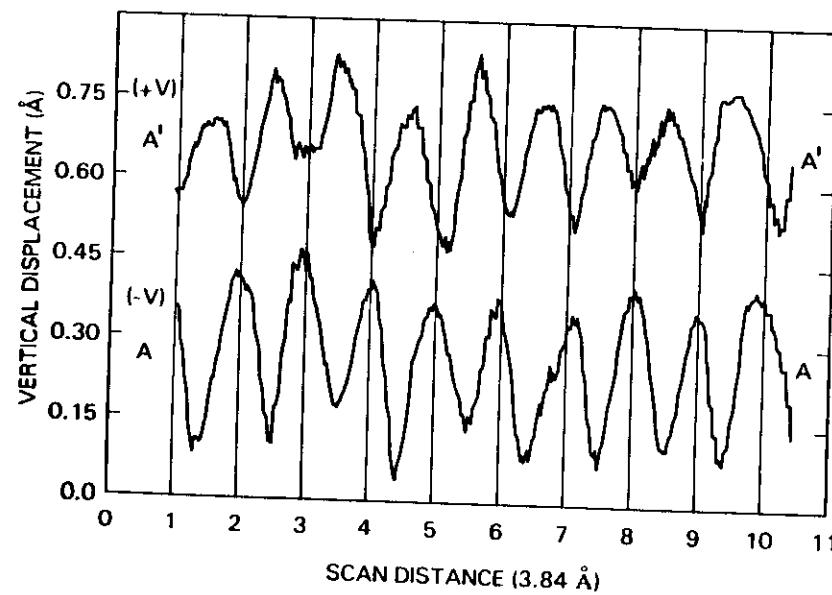
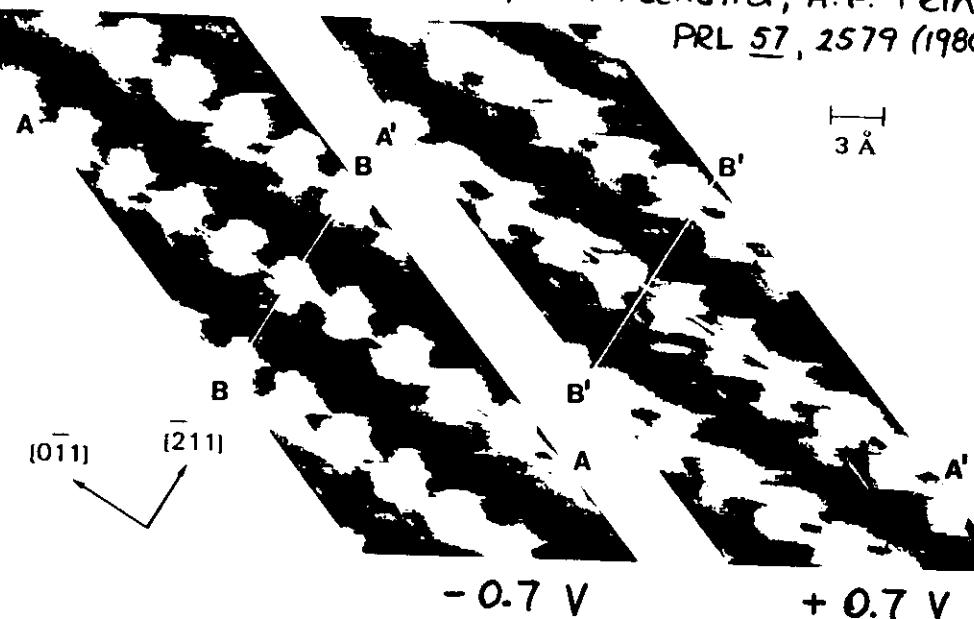


Si(III) 2x1



Si(III) 2x1



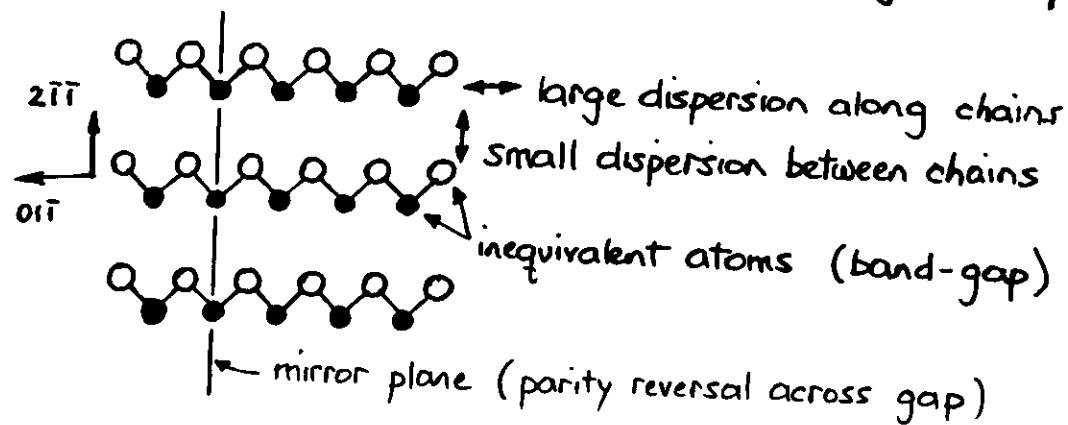
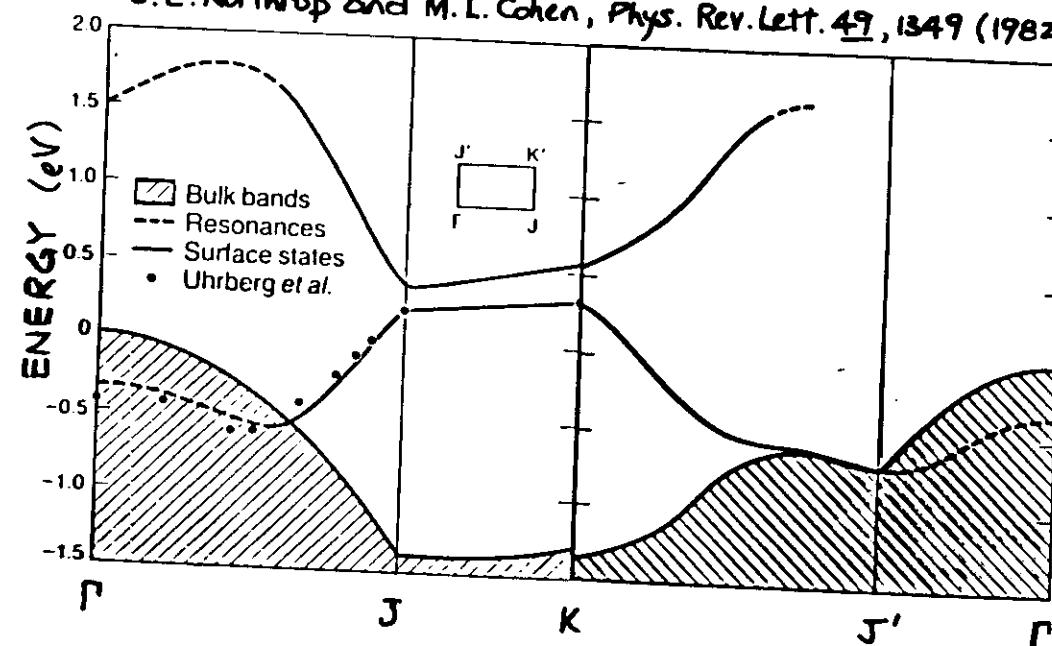


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Surface-state Bands for π -bonded chains:

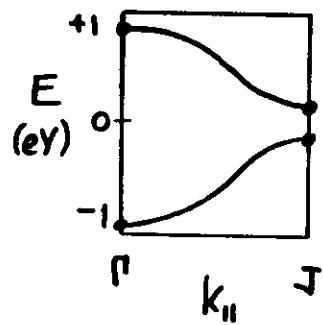
K.C. Pandey, Phys. Rev. Lett. 47, 1913 (1981)

J.E. Northrup and M.L. Cohen, Phys. Rev. Lett. 49, 1349 (1982).

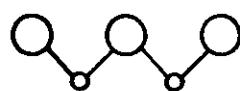


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Tight-binding wavefunctions

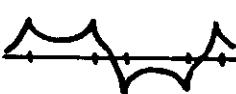
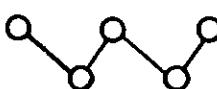
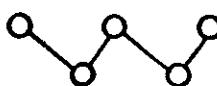


buckled chain



states centered: on atoms

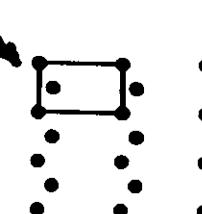
dimerized chain



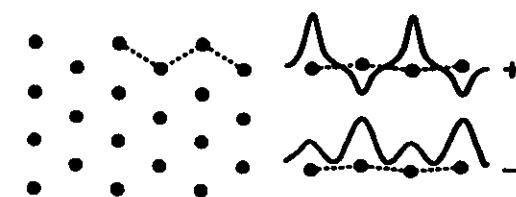
between atoms

TOP LAYER
ATOM POSITIONS

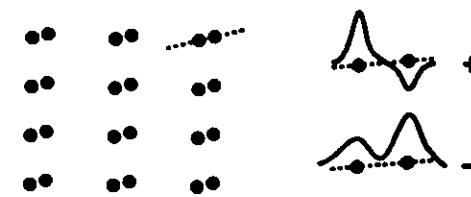
(b) = bonded chain



(b) buckled



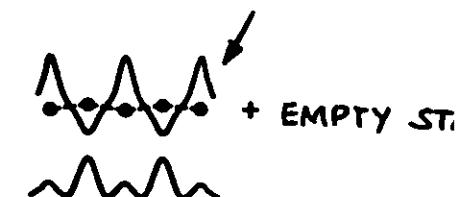
(c) π-bonded molecule



[011]
y [211]
x | [111]
z

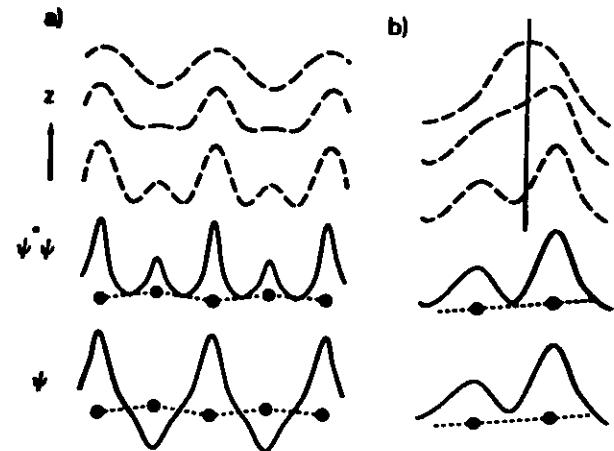
(a) = bonded chain

WAVE-FUNCT



+ EMPTY STA
- FILLED STA

Decay of State-Density ($\psi^*\psi$) with Separation from Surface

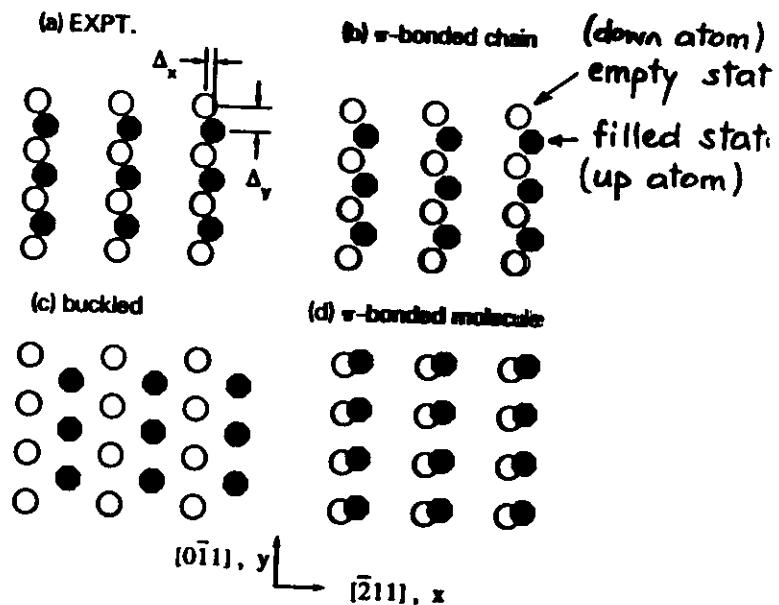


observe:

$$\Delta_x \approx 0.7 \text{ \AA}$$

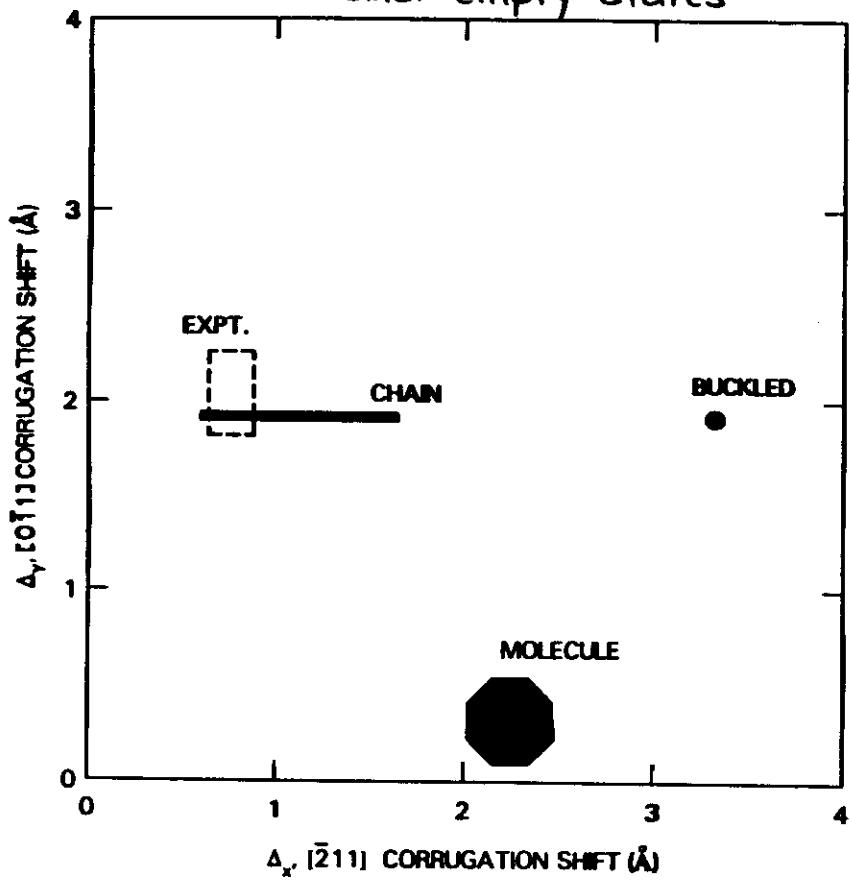
$$\Delta_y \approx 3.3 \text{ \AA}$$

Spatial location of states



STM images yield structure directly

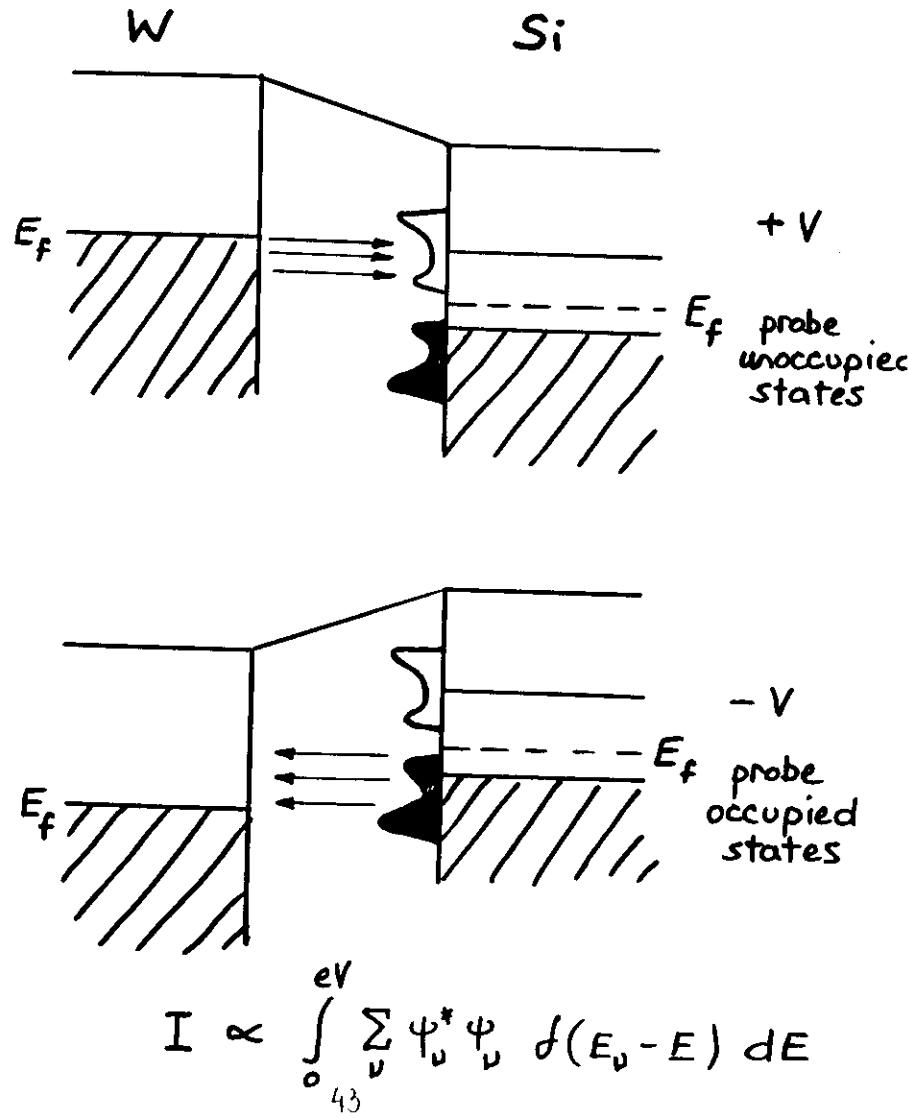
Si(111) 2x1 - Spatial shift between filled and empty states



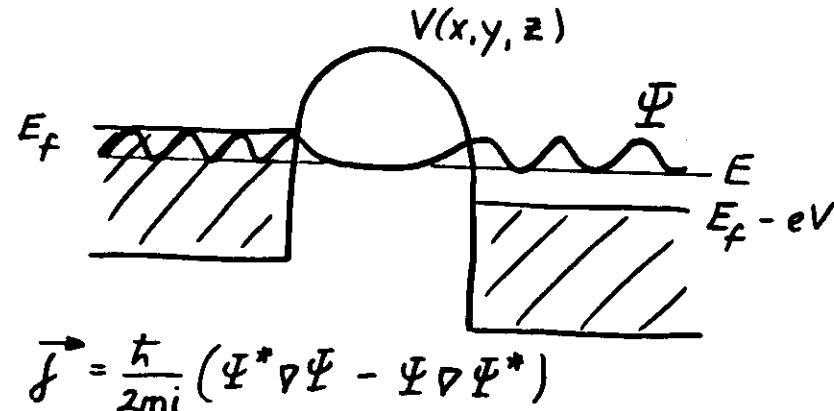
Summary:

- STM measures the electronic properties of a surface
- view surface states as linear combination of dangling bonds
- attach dangling bonds to atoms
→ connection to geometric structure

Tunneling Spectroscopy:

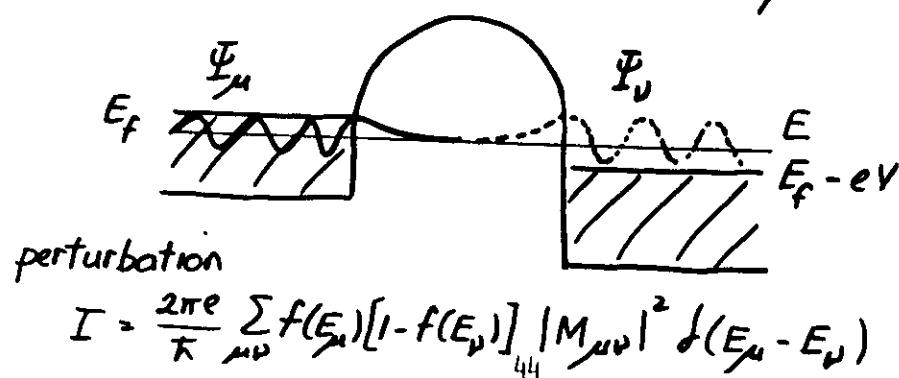


Current through Barrier



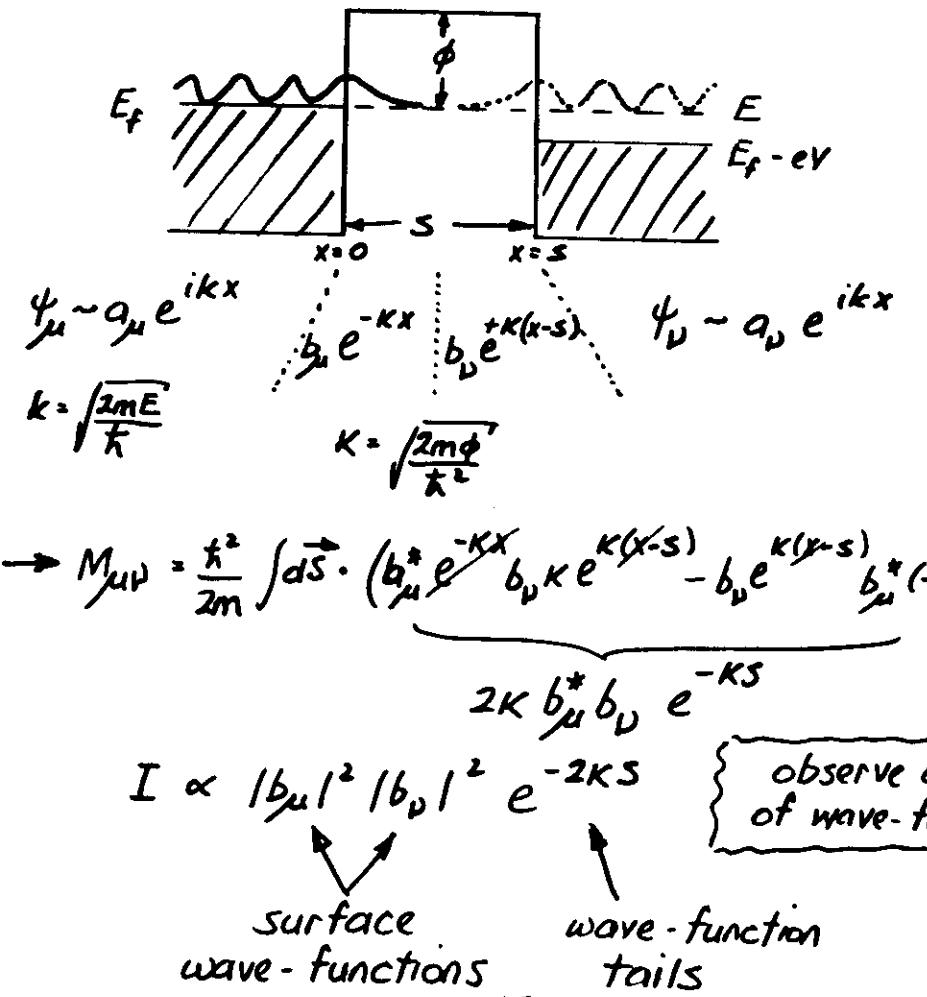
integrate over separating surface, sum over states:
(eg. Stoll, Baratoff, Seleni, Carnevali, J. Phys. C. 17, 3073 (1984),
for free-electron model with corrugated boundaries).

Bardeen: Φ_R, Φ_L known separately.



$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int d\vec{S} \cdot (\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*)$$

example:



Baratoff, Physica 127B, 143 (1983).
Tersoff and Hamann, Phys. Rev. Lett. 50, 1998 (1983).
 Phys. Rev. B 31, 805 (1985).

point probe: ψ_μ very localized, at \vec{r}_0

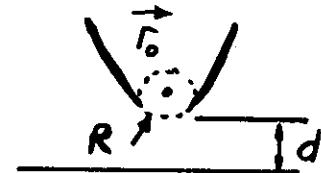
$$\Rightarrow M_{\mu\nu} \propto \psi_\nu$$

$$I \propto \sum_\nu |\psi_\nu(r_0)|^2 \delta(E_\nu - E_f)$$

$\equiv f \cdot \text{local-density-of-states}$.

* just consider f of sample, extending into vacuum.

spherical probe



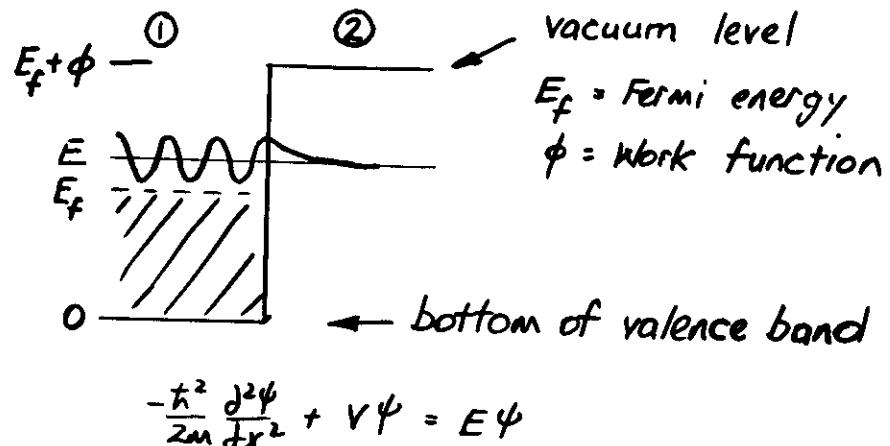
$\psi_{\text{tip}} = \psi_\mu$ = spherical waves

$$\Rightarrow I \propto \sum_\nu |\psi_\nu(r_0)|^2 \delta(E_\nu - E_f) = f(\vec{r}_0, E_f).$$

low T
low V.

STM measures f at point corresponding to center of radius-of-curvature of tip.

1-Dimensional Barrier Penetration



region ① $V=0$, $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$.

try $\psi = A e^{ikx}$ $\Rightarrow +\frac{\hbar^2}{2m} A k^2 e^{ikx} = EA e^{ikx}$
 $\Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}}$

region ② $V = E_f + \phi$, $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (E_f + \phi)\psi = E\psi$

try $\psi = B e^{-Kx}$ $\Rightarrow -\frac{\hbar^2}{2m} K^2 B e^{-Kx} = (E - E_f - \phi)B e^{-Kx}$

$\Rightarrow K = \sqrt{\frac{2m}{\hbar^2}(\phi - E')}$ *

$E' = E - E_f$
= energy relative to E_f

47

Numbers: take $E' = 0$

$$K = \sqrt{\frac{2m\phi}{\hbar^2}} = \left(\frac{2 \times 511 \times 10^{-30} \text{ eV} \times 4.5 \text{ eV}}{(1973 \text{ eV}\cdot\text{\AA})^2} \right)^{1/2} = 1.1 \text{ \AA}^{-1}$$

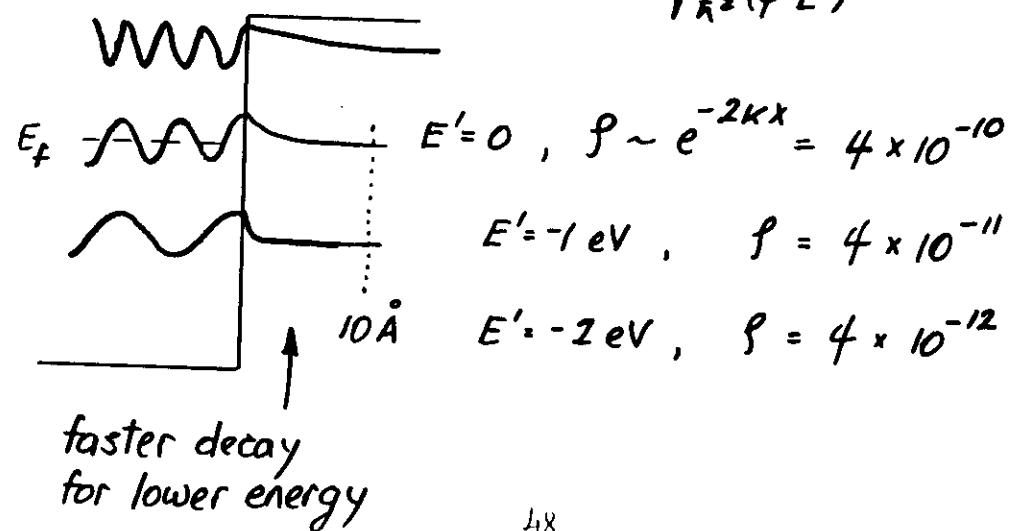
$$f = \text{state-density} = 4^* 4 \sim e^{-2Kx}$$

$$\Delta x = 1 \text{ \AA} \Rightarrow \frac{f_{\text{new}}}{f_{\text{old}}} = \frac{e^{-2K(x+\Delta x)}}{e^{-2Kx}} = e^{-2K(1 \text{ \AA})} \approx 0.1$$

an order-of-magnitude change for each \AA.

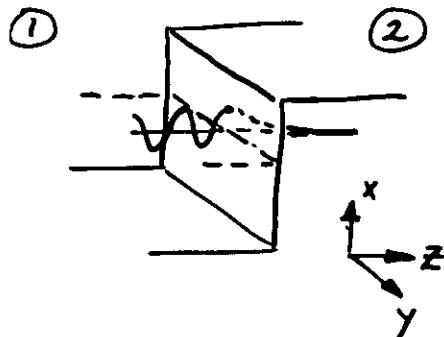
Energy dependence: $E' \neq 0$

$$K = \sqrt{\frac{2m}{\hbar^2}(\phi - E')}$$



48

3-Dimensional Planar Barrier Penetration



$$V = V(z)$$

$$\Psi = \psi_{||}(x, y) \psi_{\perp}(z)$$

$$-\frac{\hbar^2}{2m} \left[\psi_{\perp} \left(\frac{\partial^2 \psi_{||}}{\partial x^2} + \frac{\partial^2 \psi_{||}}{\partial y^2} \right) + \psi_{||} \frac{\partial^2 \psi_{\perp}}{\partial z^2} \right]$$

$$+ V(z) \psi_{||} \psi_{\perp} = E \psi_{||} \psi_{\perp}$$

write $E = E_{||} + E_{\perp}$

$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi_{||}}{\partial x^2} + \frac{\partial^2 \psi_{||}}{\partial y^2} \right) = E_{||} \psi_{||} \Rightarrow \psi_{||} = A e^{i \vec{k}_{||} \cdot (\vec{x}, \vec{y})}$$

$$k_{||} = \sqrt{\frac{2mE_{||}}{\hbar^2}}$$

and $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_{\perp}}{\partial z^2} + V(z) \psi_{\perp} = E_{\perp} \psi_{\perp}$

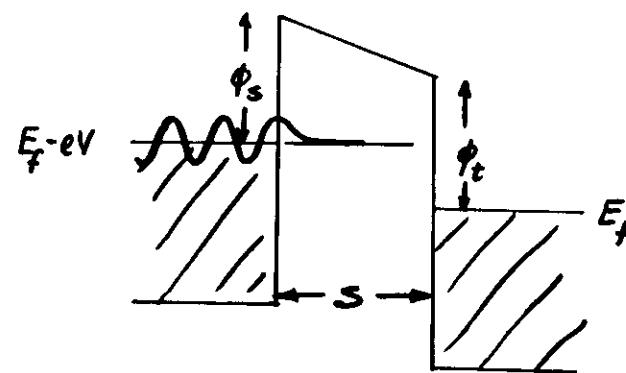
$$E_{\perp} = E - E_{||} = E - \frac{\hbar^2 k_{||}^2}{2m}$$

region (2) $\psi_{\perp} = A e^{-Kz}$

$$K = \sqrt{\frac{2m}{\hbar^2} \left(\phi - E' + \frac{\hbar^2 k_{||}^2}{2m} \right)} *$$

states with large $k_{||}$ decay faster (for $E = \text{const.}$)

Trapezoidal Barrier (finite voltage)



sample

tip

($k_y = 0$)

$$I \propto \int \rho_s(E) dE$$

$$\rho_s \propto e^{-2Kz} = e^{-2Ks}$$

$$K = \sqrt{\frac{2m}{\hbar^2} (\phi - E')}$$

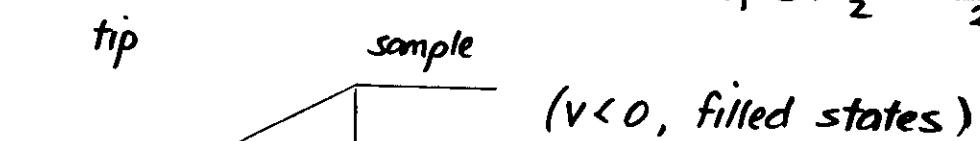
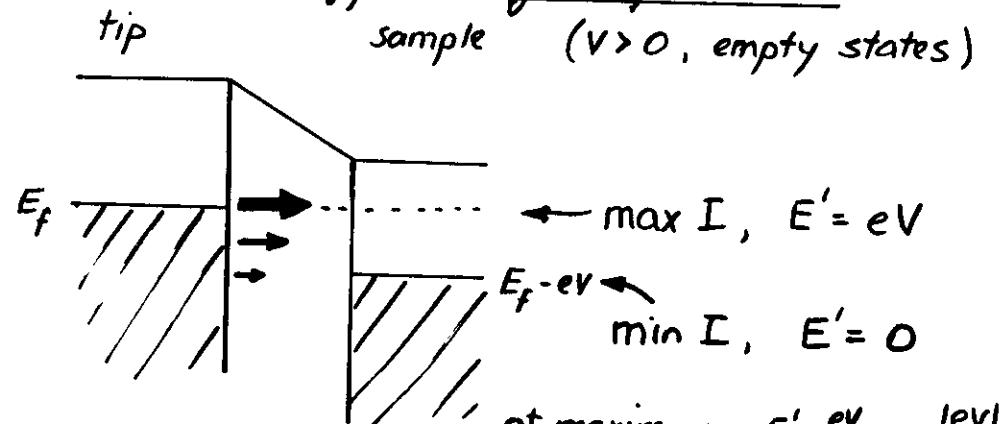
trap.
barrier $\phi \rightarrow \bar{\phi} = \frac{\phi_s + \phi_t + eV}{2} = \phi_{st} + \frac{eV}{2}$
(WKB)

for $E' = 0$.

$$\therefore K = \sqrt{\frac{2m}{\hbar^2} \left(\phi_{st} - E' + \frac{eV}{2} \right)} *$$

ϕ_{st} = average
work-fcn betw
tip + sample

Effect of energy + voltage dependence

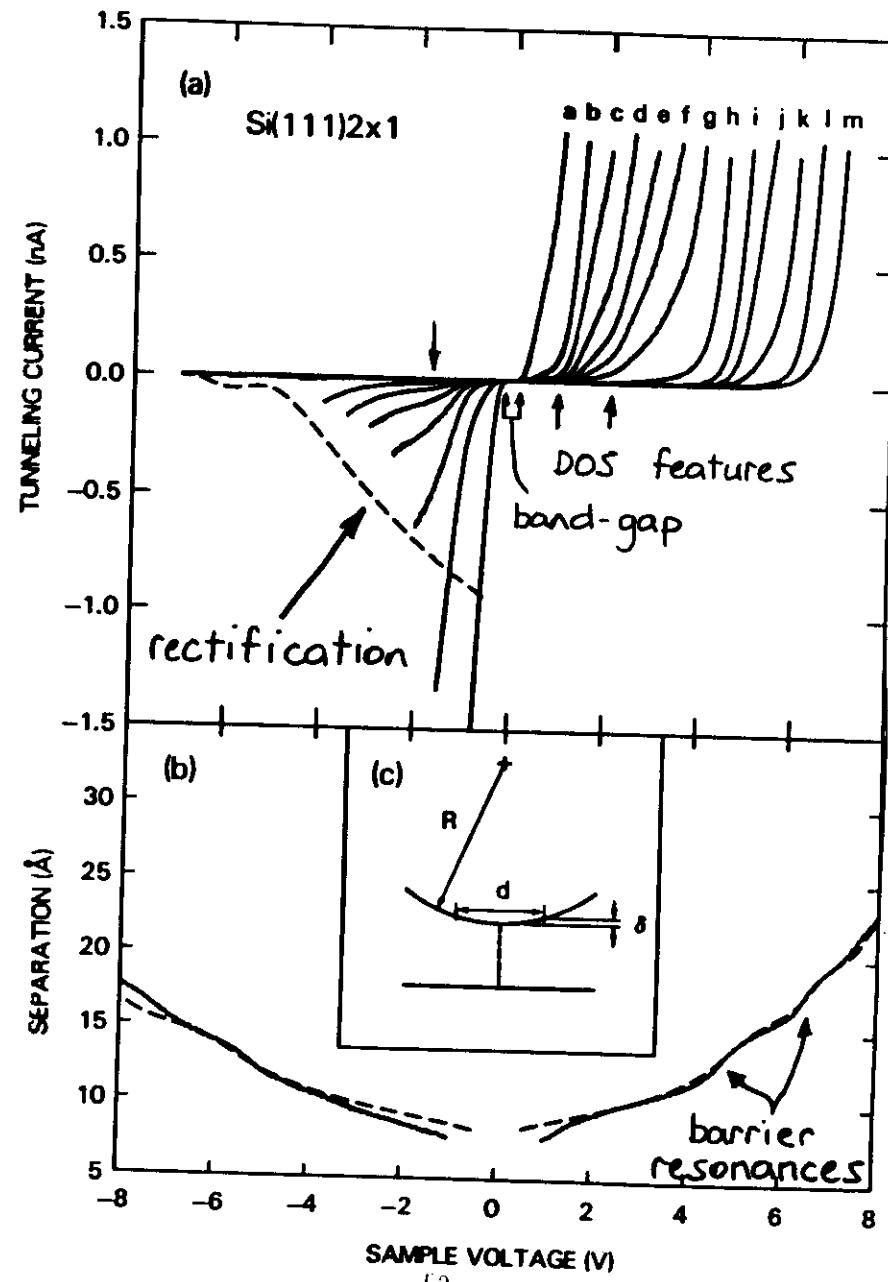


$$I \propto \int f_s(E, z=s) dE = \int f_0(E) e^{-2kS} dE$$

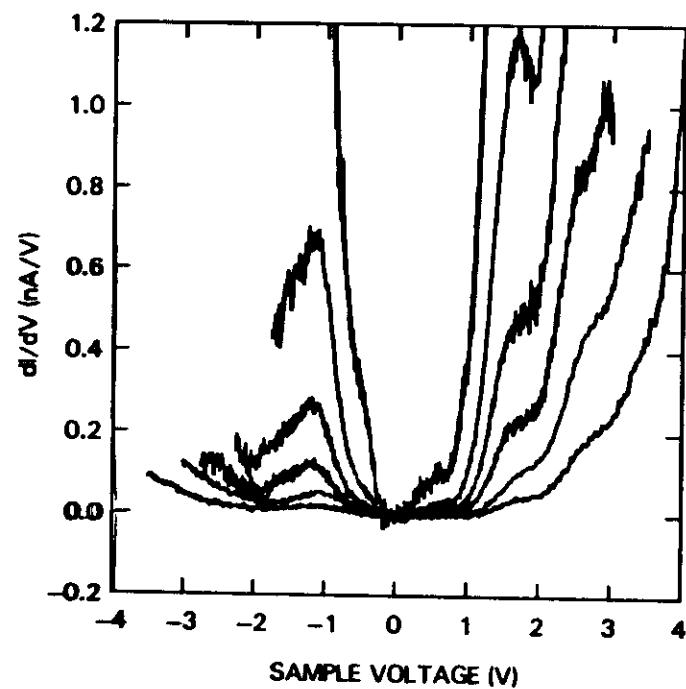
$$\rightarrow \begin{cases} f_0(eV) e^{-2kS}, & V > 0 \\ f_0(E=0) e^{-2kS}, & V < 0 \end{cases}$$

$K = \sqrt{\frac{2m}{\hbar^2} \left(\phi_{st} - \frac{levl}{2} \right)}$

51) Current through tunnelling occupied states!



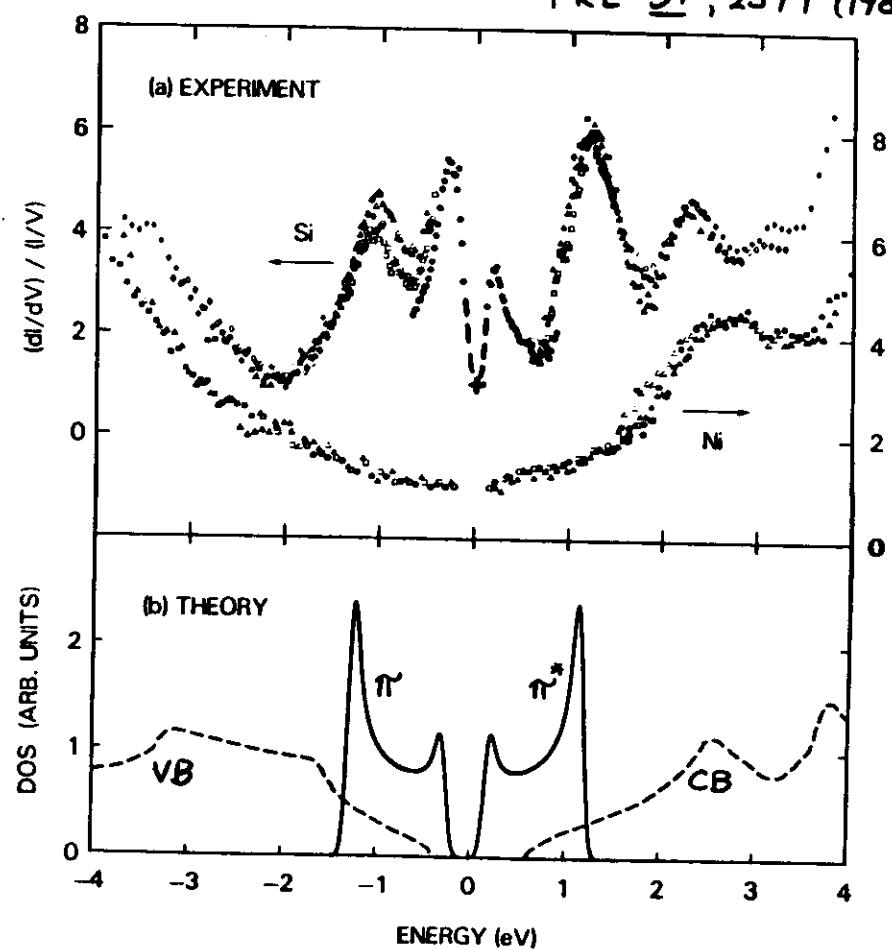
1st- Derivative Spectra



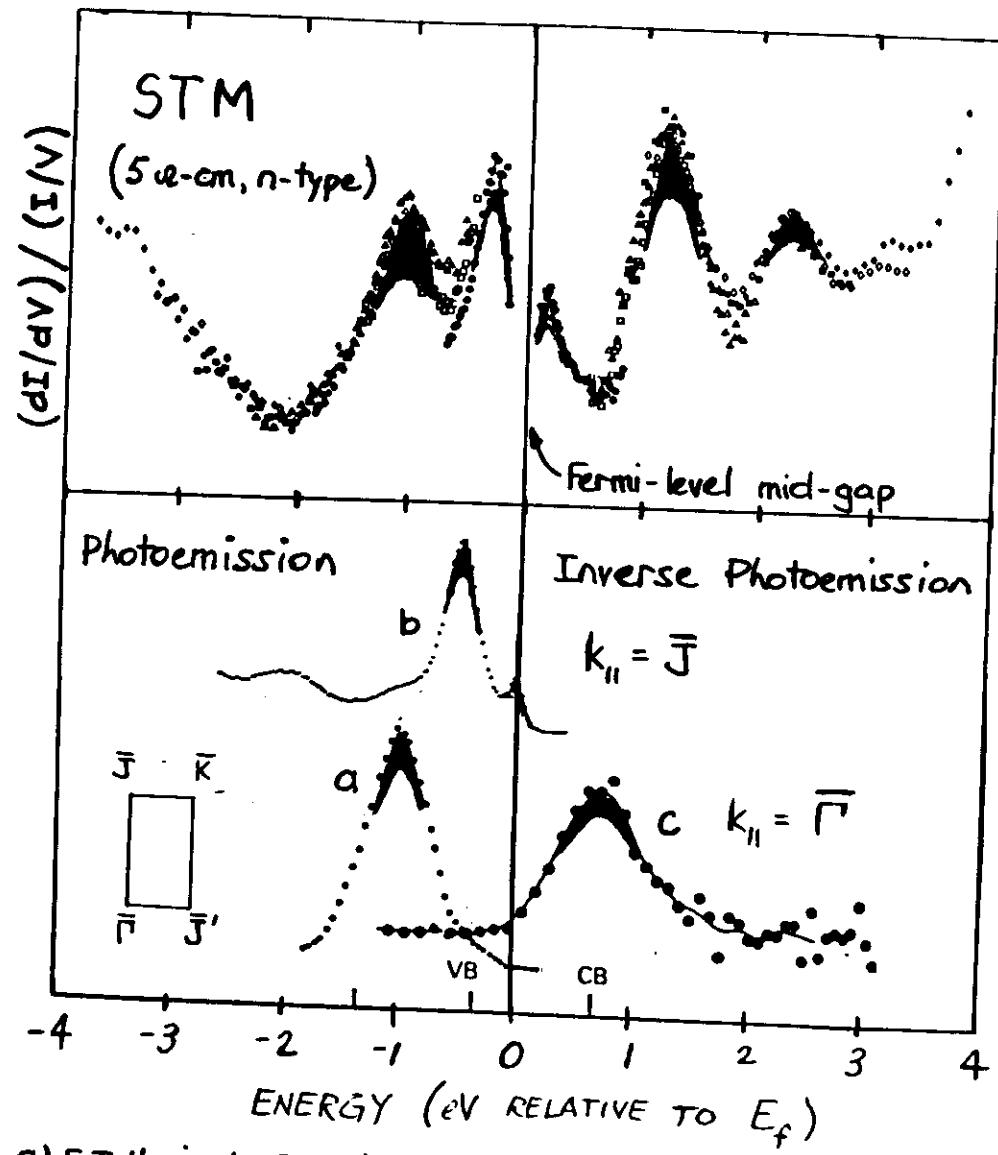
53

Si (111) - 2x1

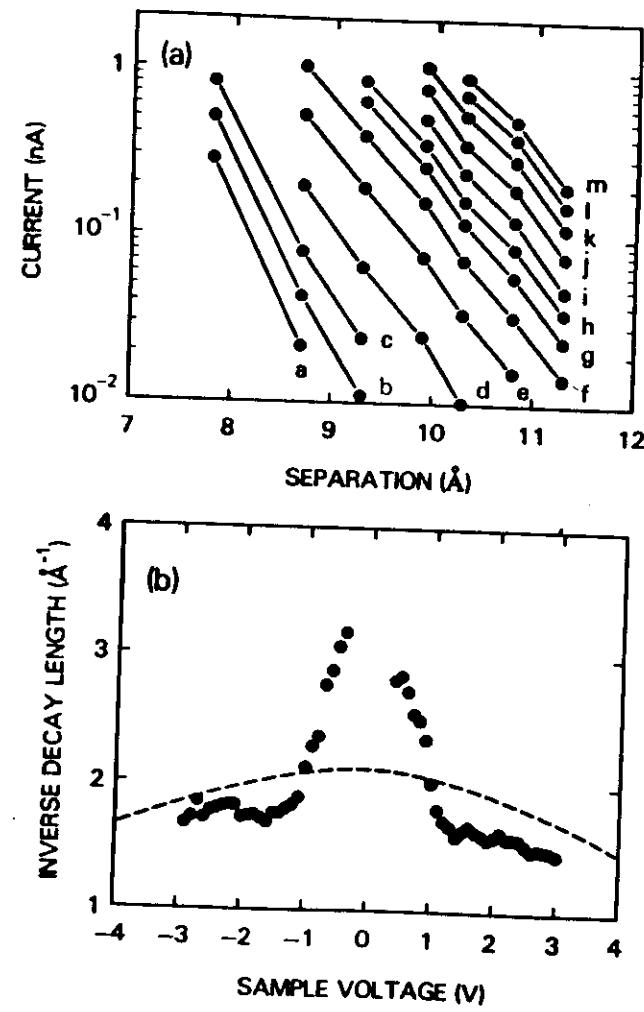
J. A. Stroscio, R. M. Feenstra, A. P. Fein
PRL 57, 2579 (1986)

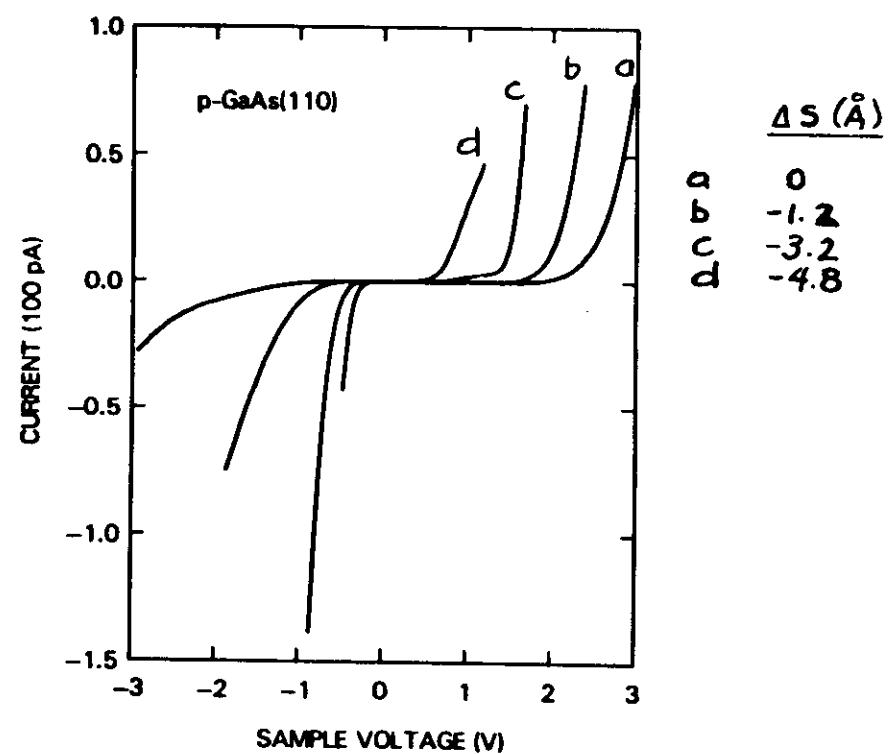


Surface bands - π , π^* (1-D tight-binding model)
Bulk bands - VB, CB (Chelikowsky and Cohen
Phys. Rev. B 14, 556 (1974))



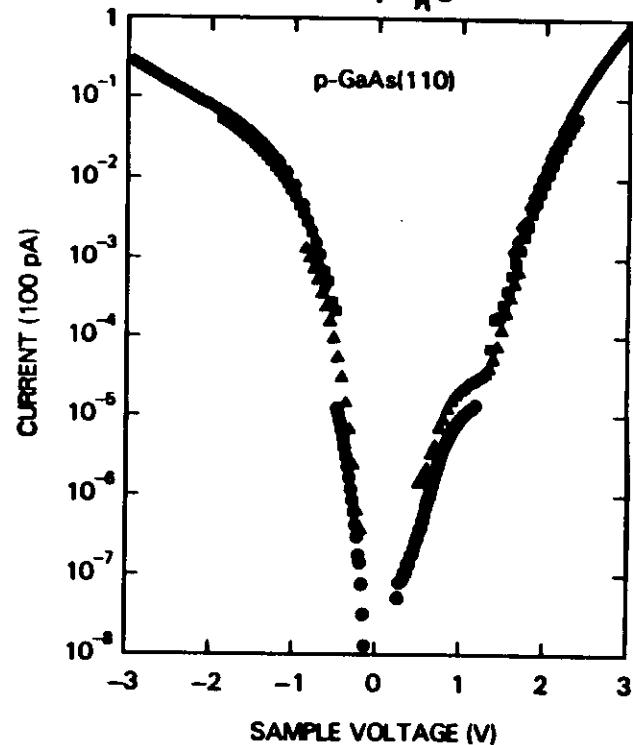
- a) F.J. Himpsel, P. Heimann, D.E. Eastman, Phys. Rev. B 24, 2003 (1981)
 b) P. Mårtensson, A. Criventi, G. Hansson, Phys. Rev. 32, 6959 (1985)
 c) D. Straub, L. Ley, F.J. Himpsel, Phys. Rev. Lett. 54, 142 (1985)





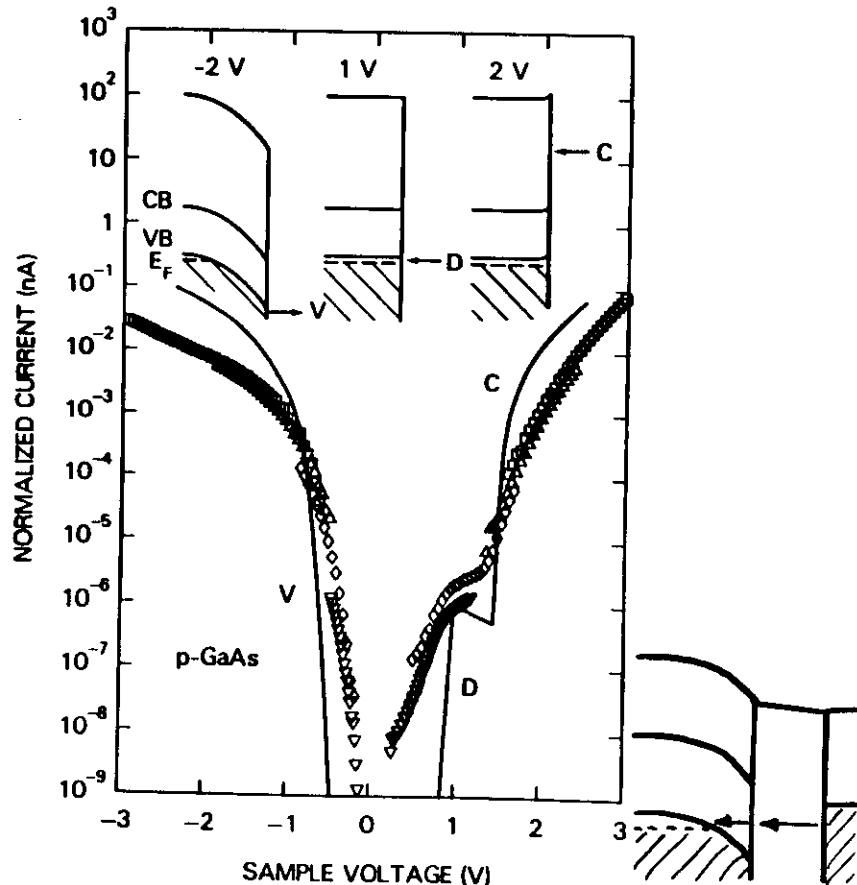
$$\text{Normalized Current} = I e^{2K\phi S}$$

$$K = \sqrt{\frac{2m\phi}{\hbar^2}} = 1.1 \text{ \AA}^{-1}, \quad \bar{\phi} = 4.5 \text{ eV}$$

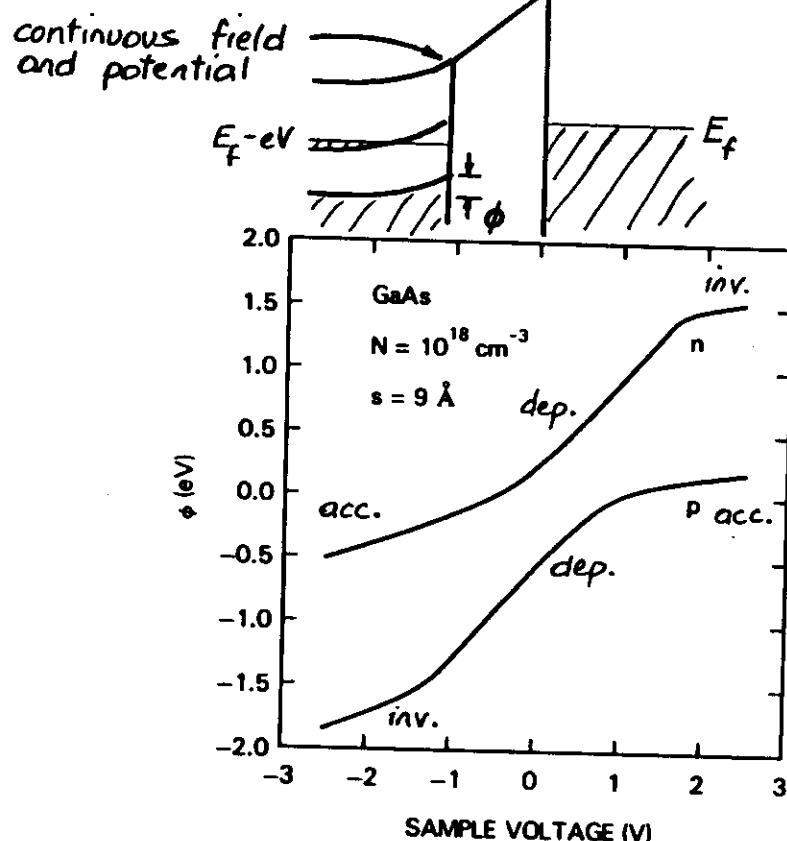


Feenstra + Strascia, JVST B, Jul/Aug (1987).

p-GaAs (110) clean surface



Electrostatics: Schottky model

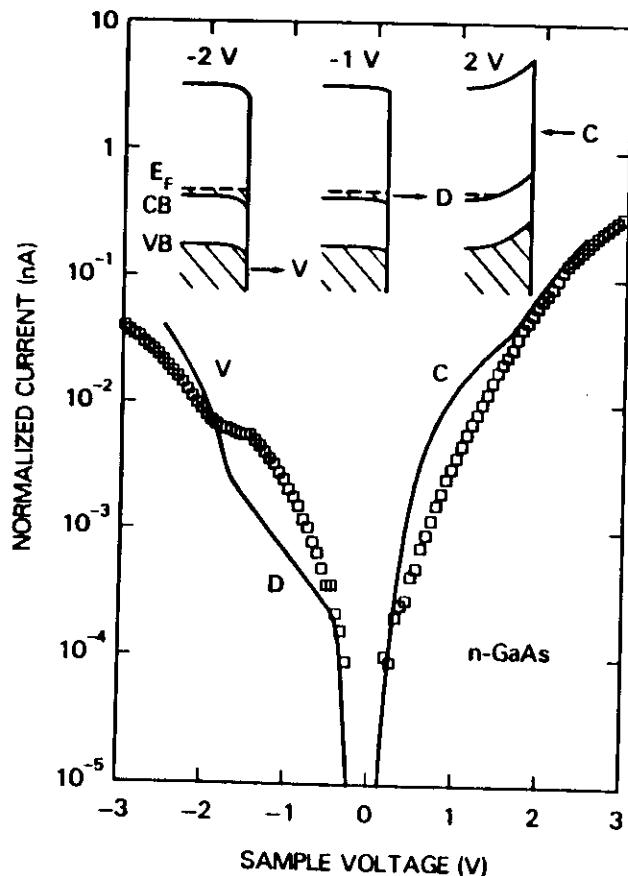


Theory: following Bono + Good, Surf. Sci. 175, 415 (1986)

- parabolic bands, WKB

plus: band-bending in semiconductor,
tunneling through semiconductor.

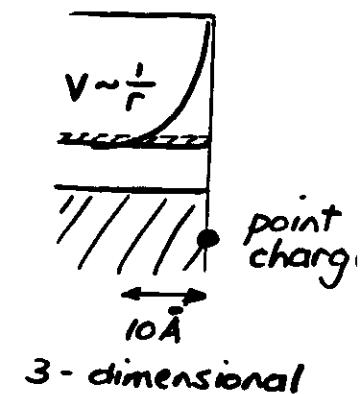
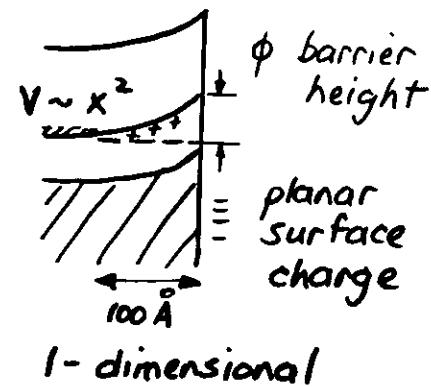
n-GaAs - clean surface



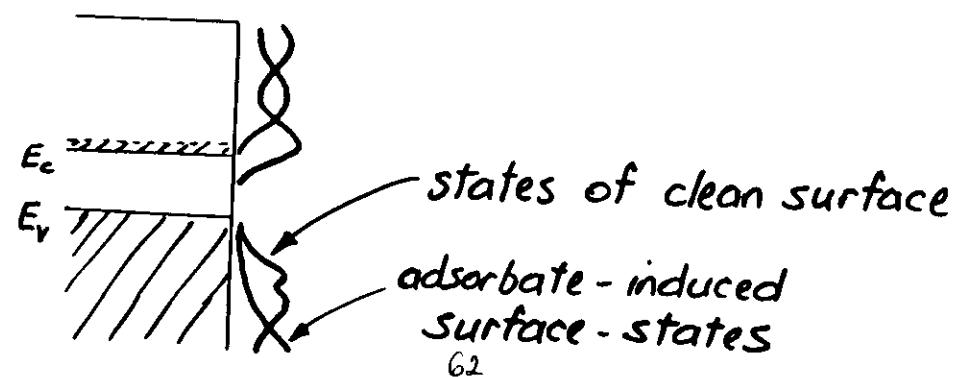
61

Spectroscopy of Adsorbates on Semiconductors

1. Electrostatics (band bending)

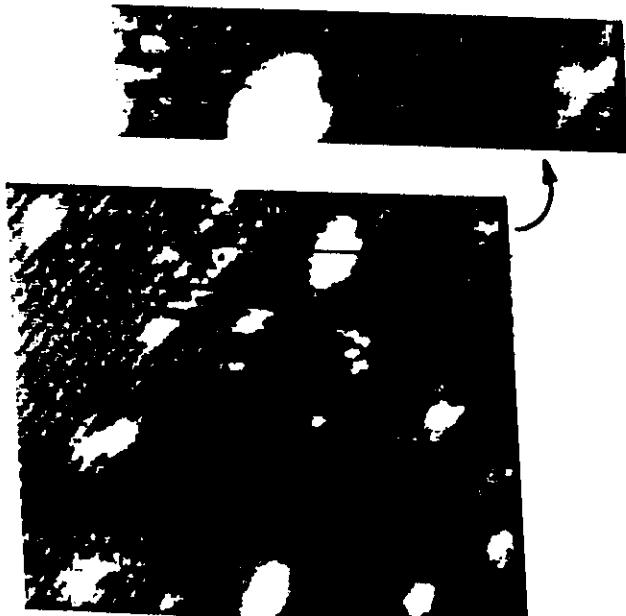


2. Changes in State-Density



O/GaAs (110) 120 L

~.003 Monolayer

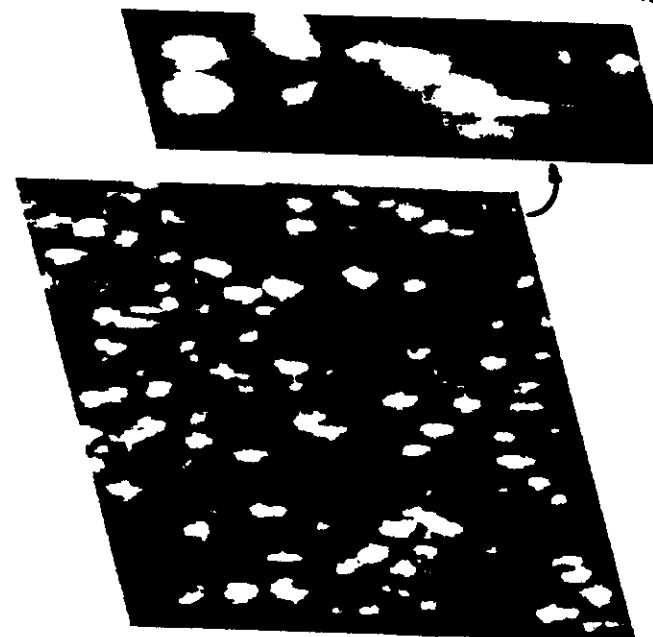


$400 \times 400 \text{ \AA}^2$

O/n-GaAs (110)

1480 L

~.01 Monolayer

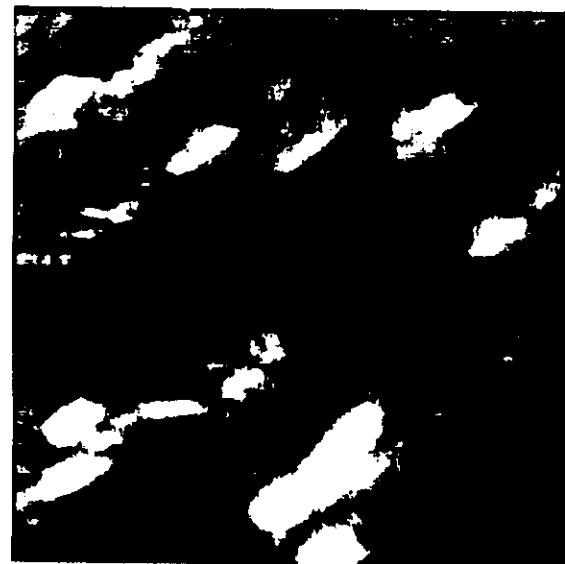


$400 \times 400 \text{ \AA}^2$

63

64

O/GaAs



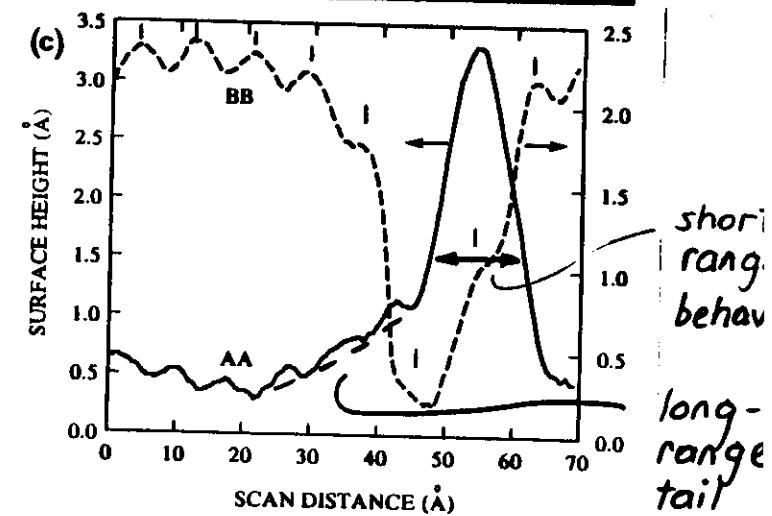
- 2.5 V

filled
states



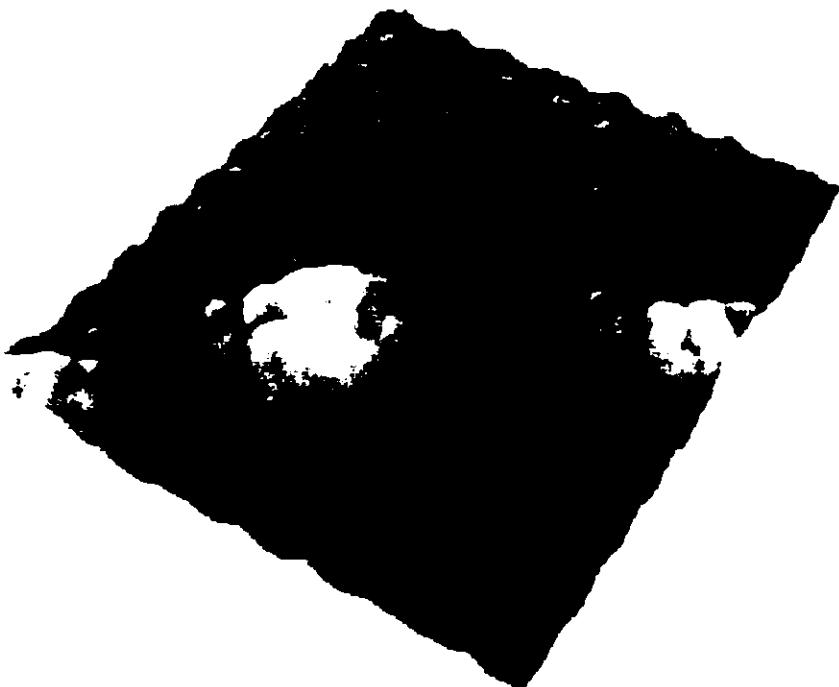
+ 1.5 V

empty
states



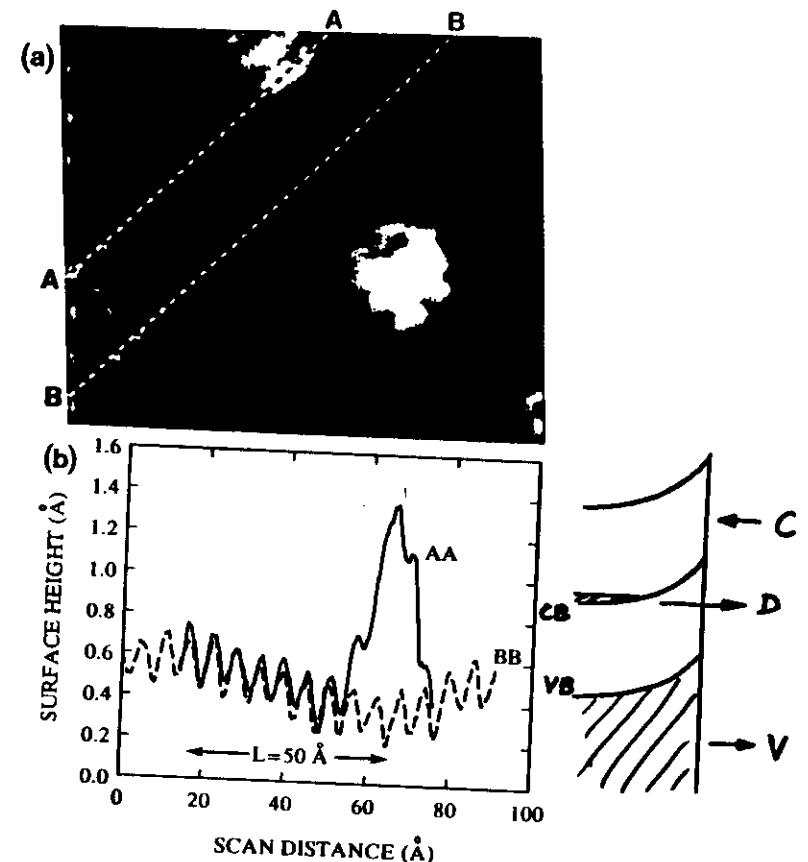
J. Stroscio, R. Feenstra, A. Fein, Phys. Rev. Lett. 58, 1668 (1987).

n -GaAs (110) - defect



67

Long-range (electrostatic) effect:



Screened
Coulomb
potential:

$$\frac{e^{-r/L}}{r}$$

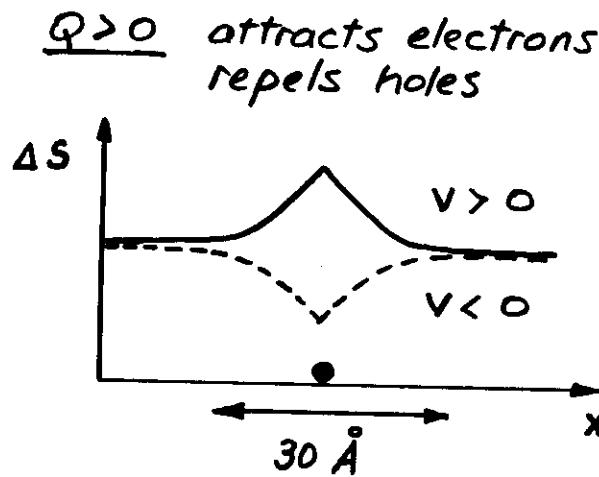
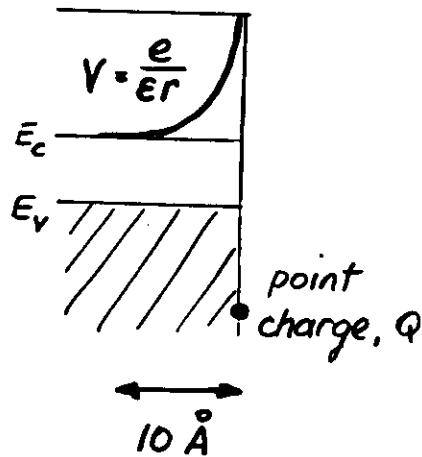
$$L = \frac{\epsilon kT}{ne^2} = 56 \text{ \AA}$$

$$n = 1 \times 10^{18} \text{ cm}^{-3}$$

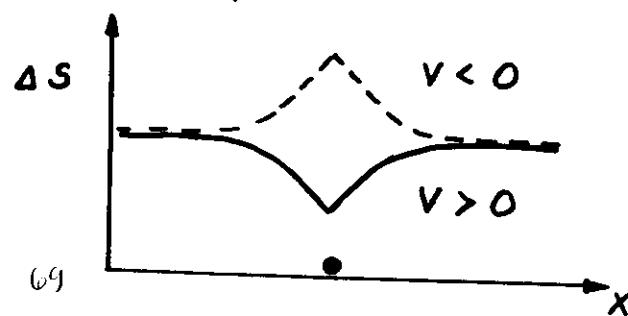
68

Fig 3

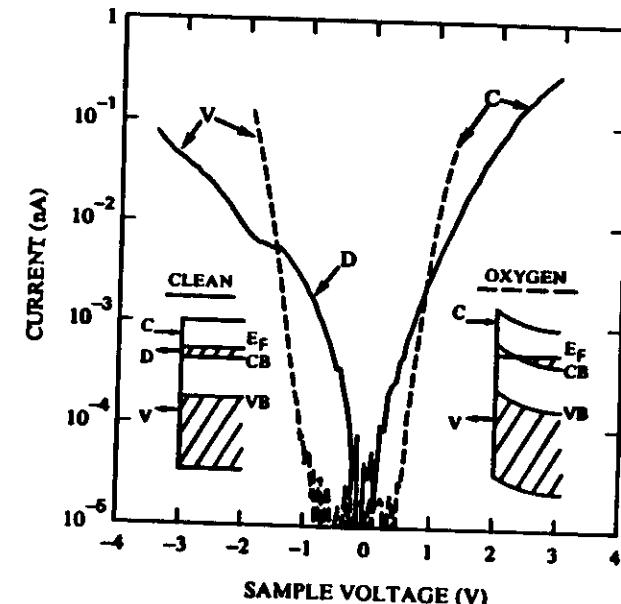
Observation of Charge with the STM (Local band-bending)



$Q < 0$ attracts holes repels electrons



n-GaAs

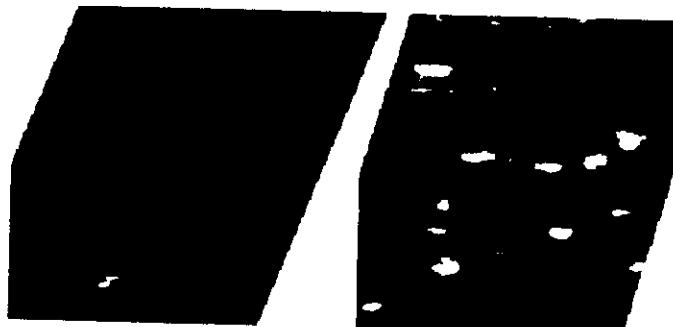


band-bending \rightarrow increased VB density
decreased CB density
(negatively charged defects)

Sb/GaAs (110)

(ML = monolayer)

.03 ML



.2 ML



.65 ML



1 ML

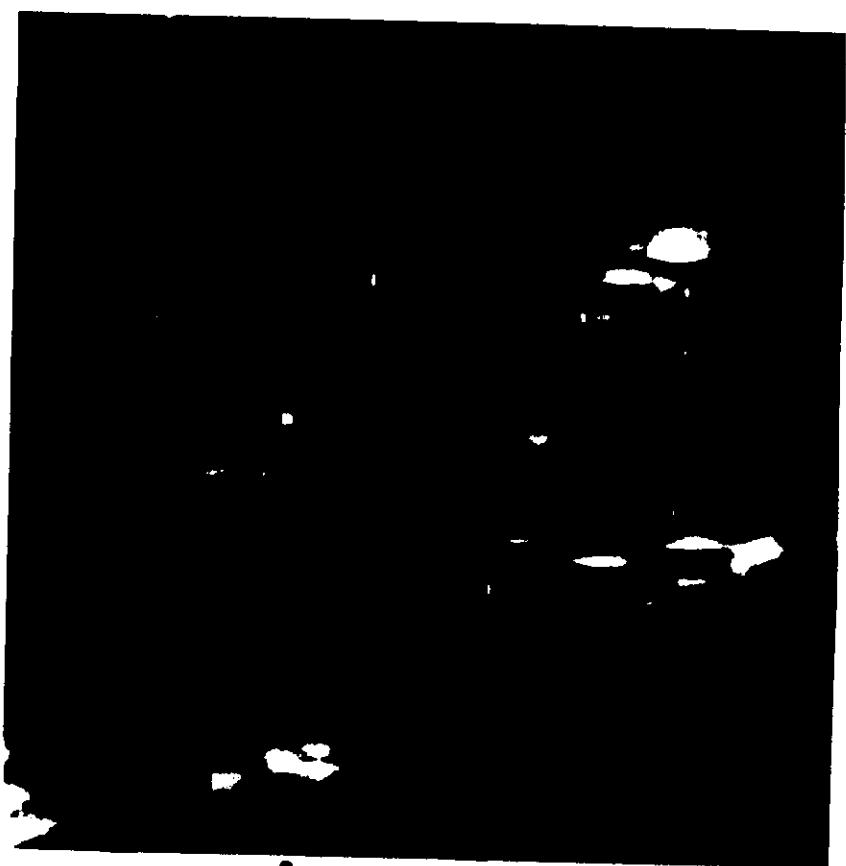


001
↑ T10

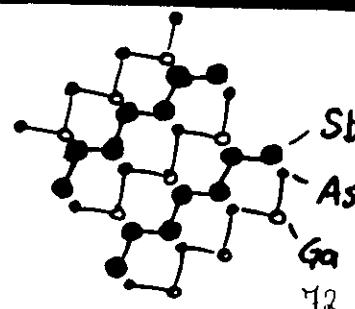
160 Å

71

Sb/GaAs (110) - ordered cluster



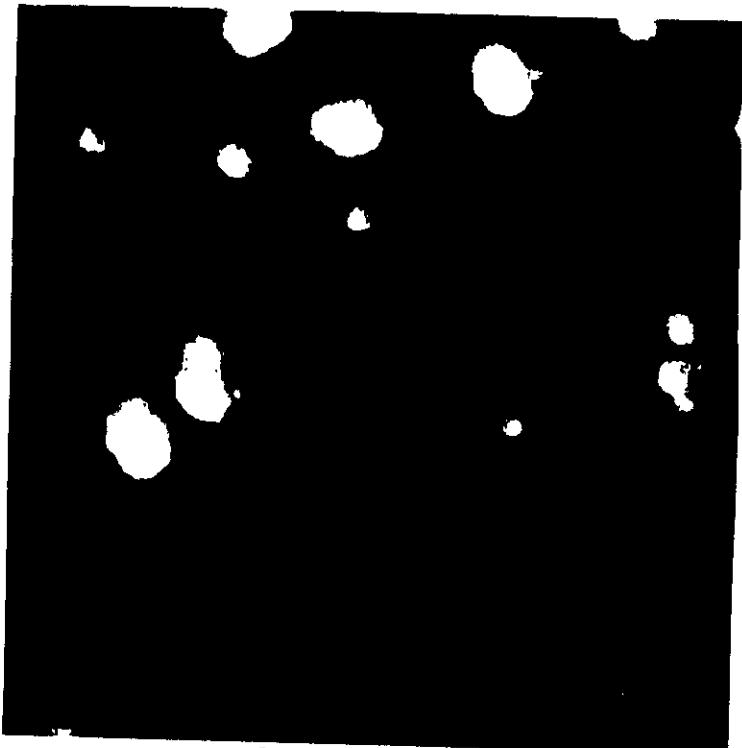
5 Å



72
images are
consistent with model

Sb/GaAs (110) 1×1 overlayer

1 ML

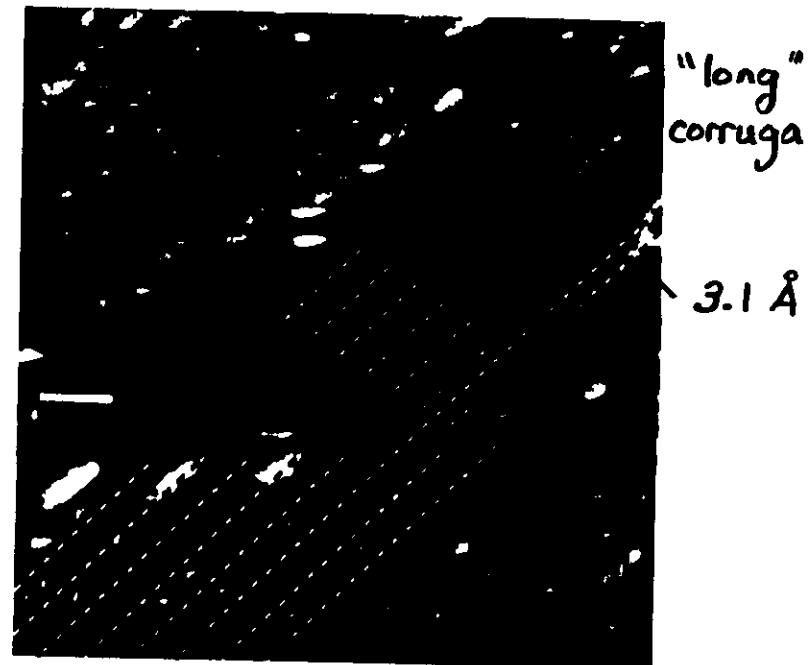


001 $\overrightarrow{11}$
10 Å

10 Å

001 $\overrightarrow{110}$

Sb/GaAs registration

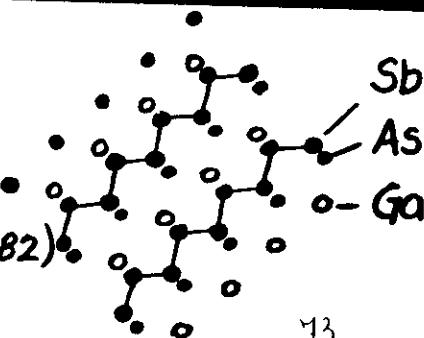


LEED:

Duke, et.al.

Phys. Rev. B

26, 803 (1982)



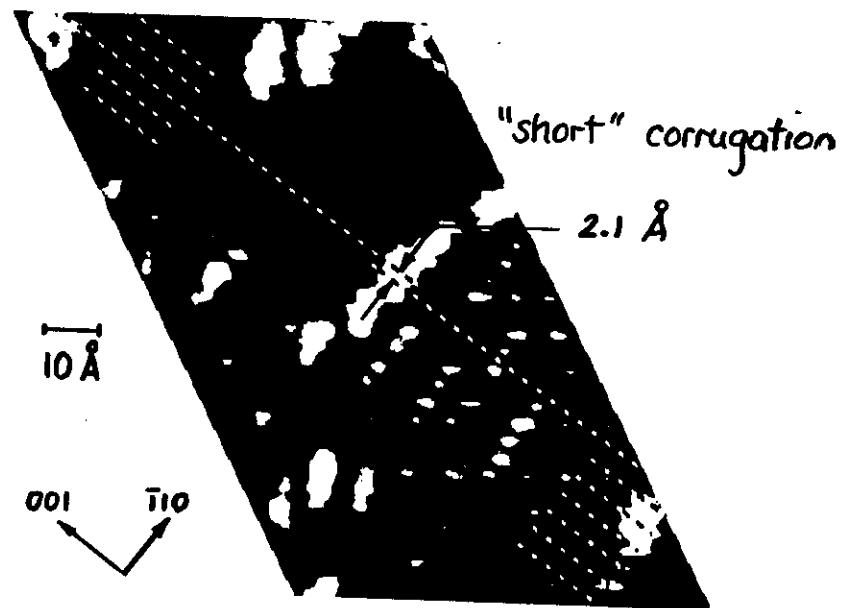
73

- two inequivalent
Sb atom per cell

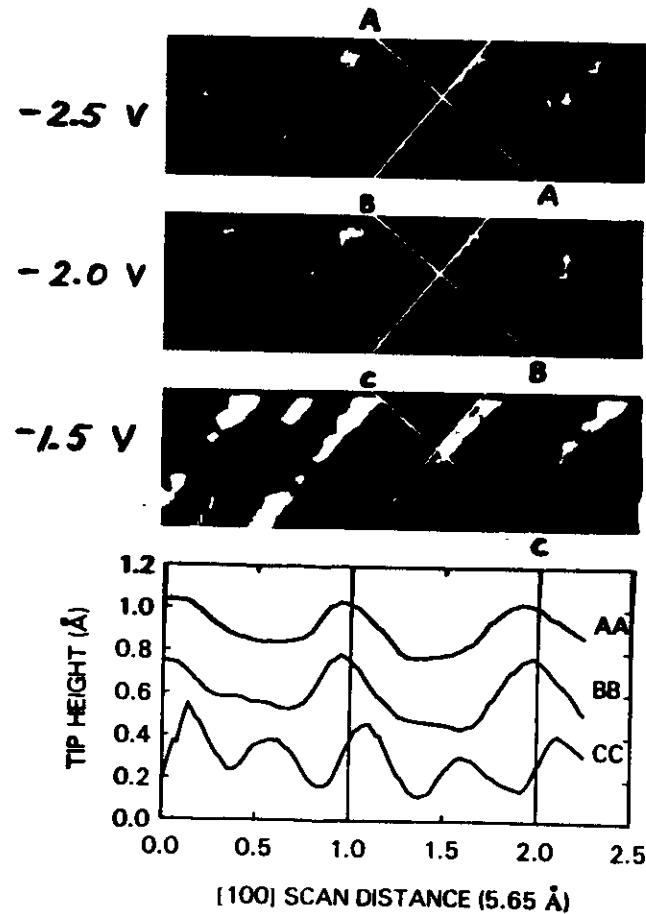
- filled dangling
bonds.

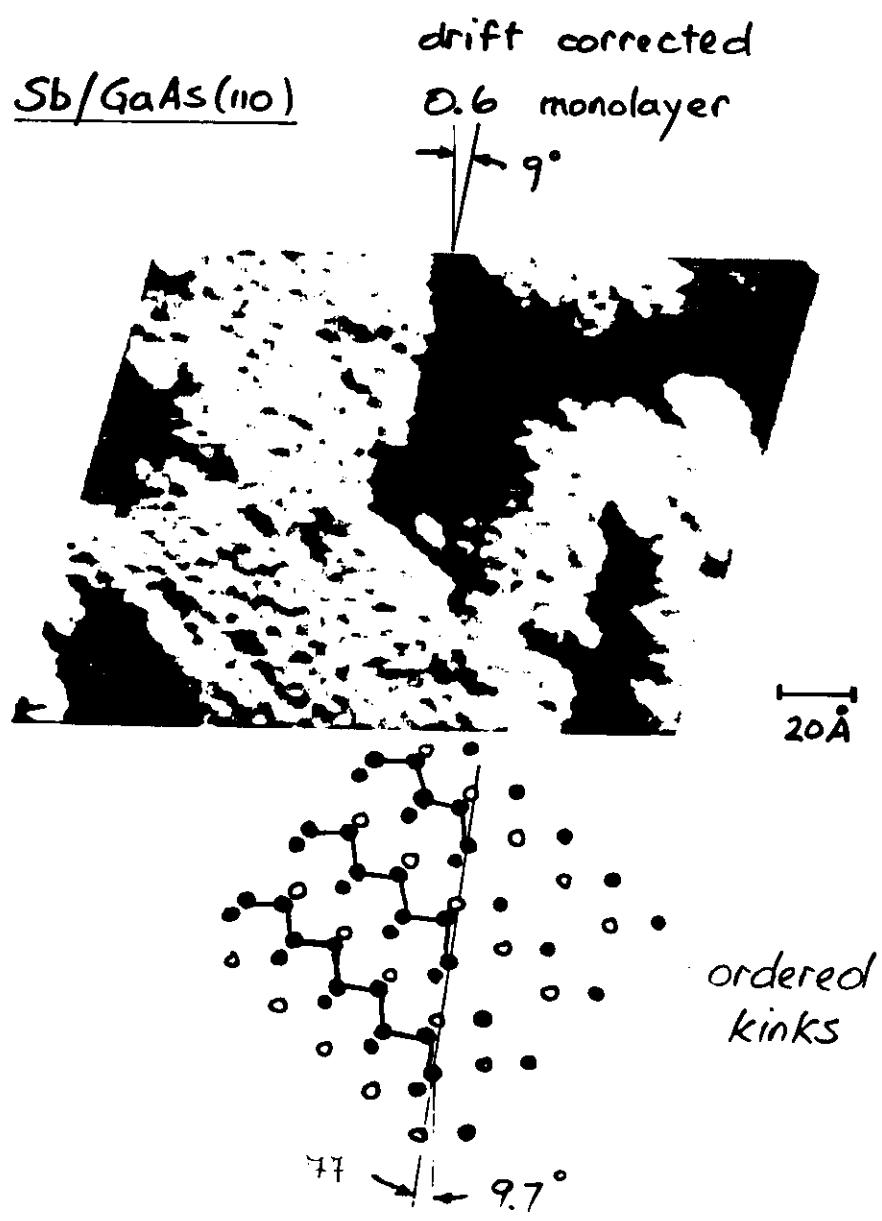
74

Sb/GaAs registration

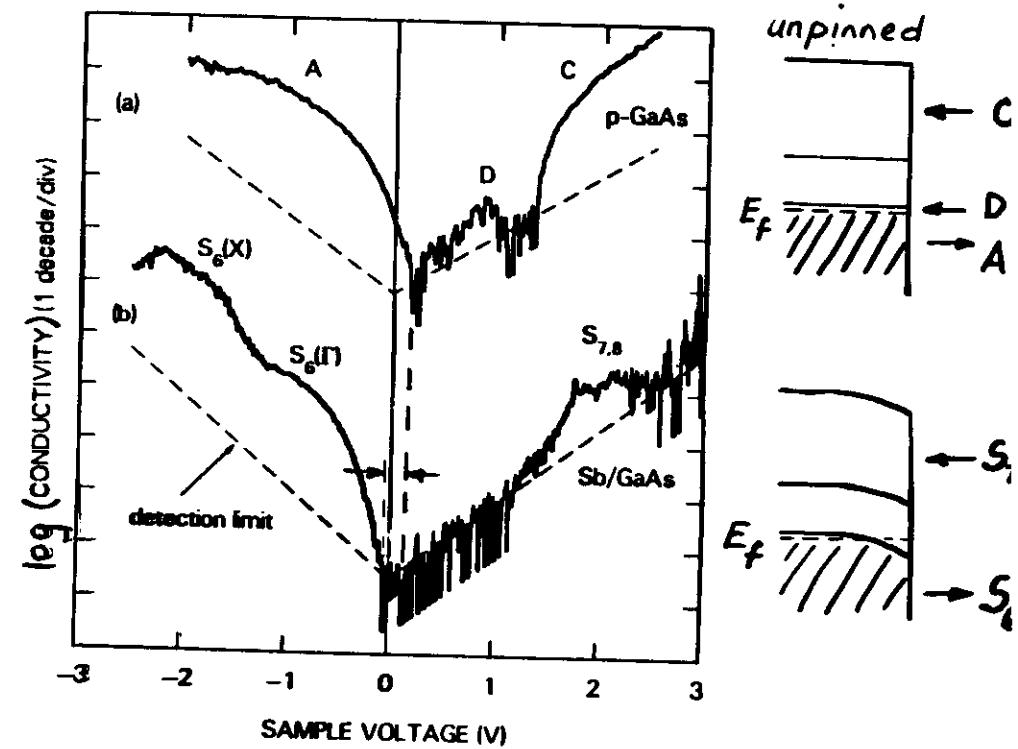


Sb/GaAs (110) - voltage dependence



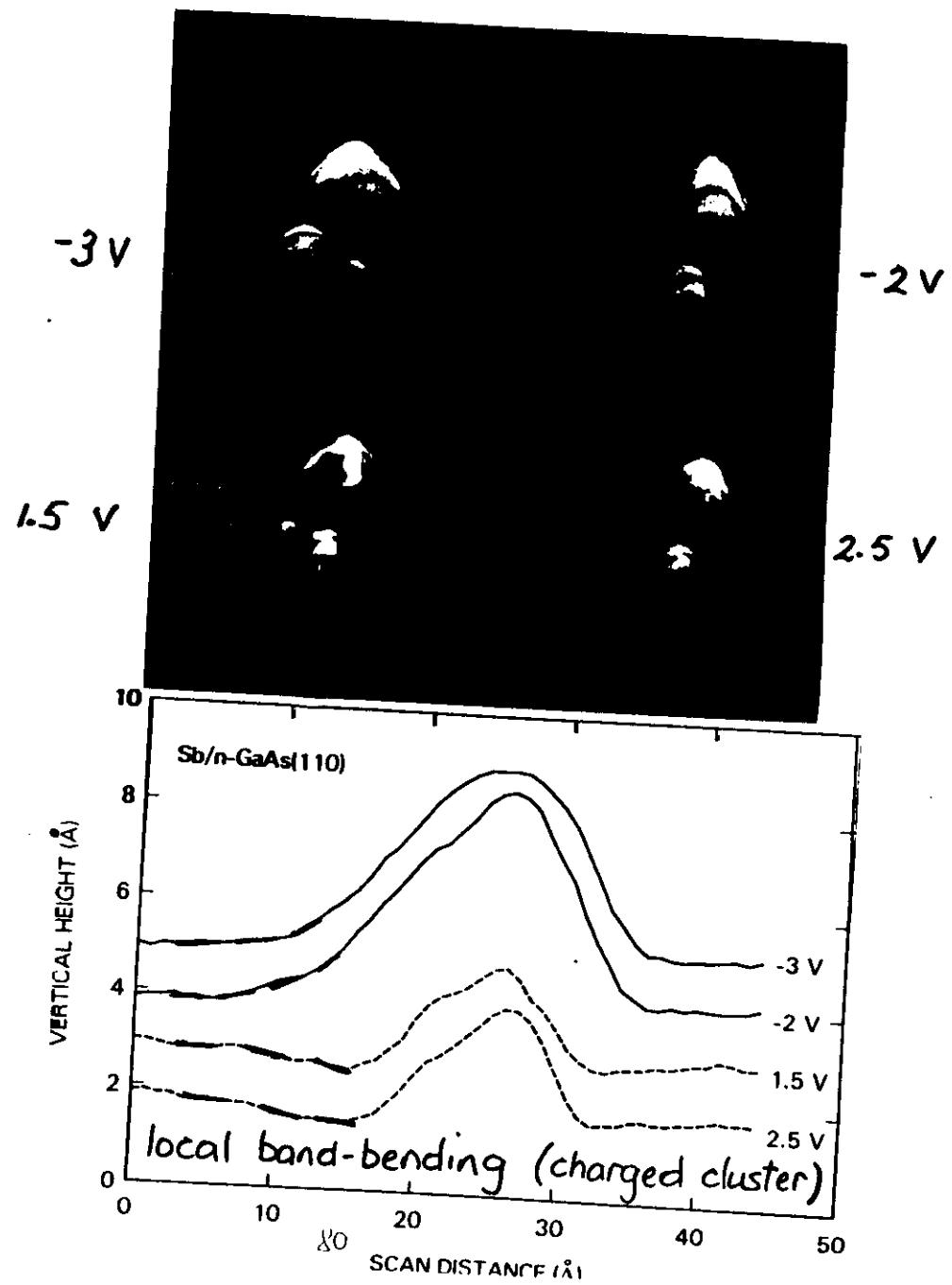
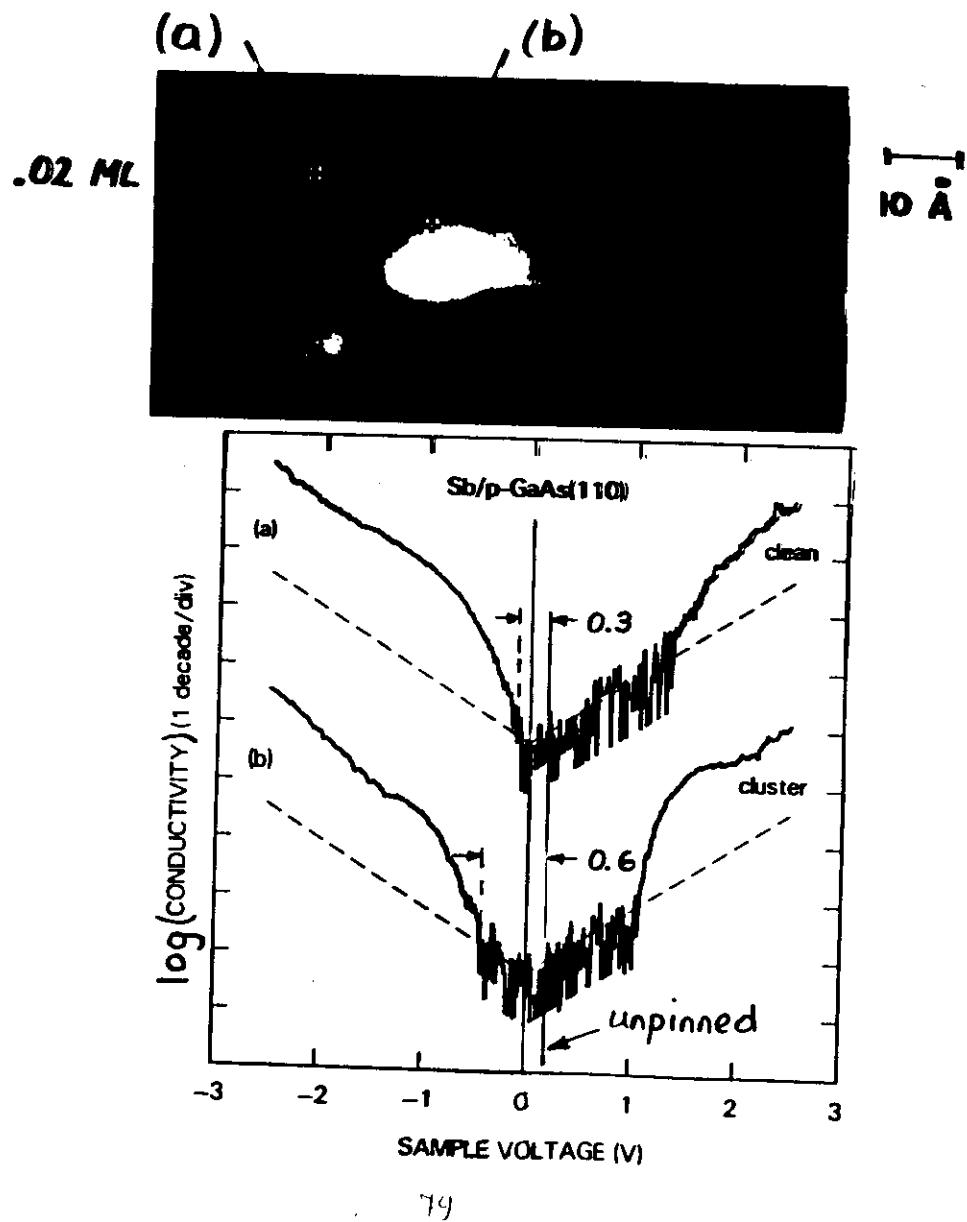


Conductivity at constant z (log scale)



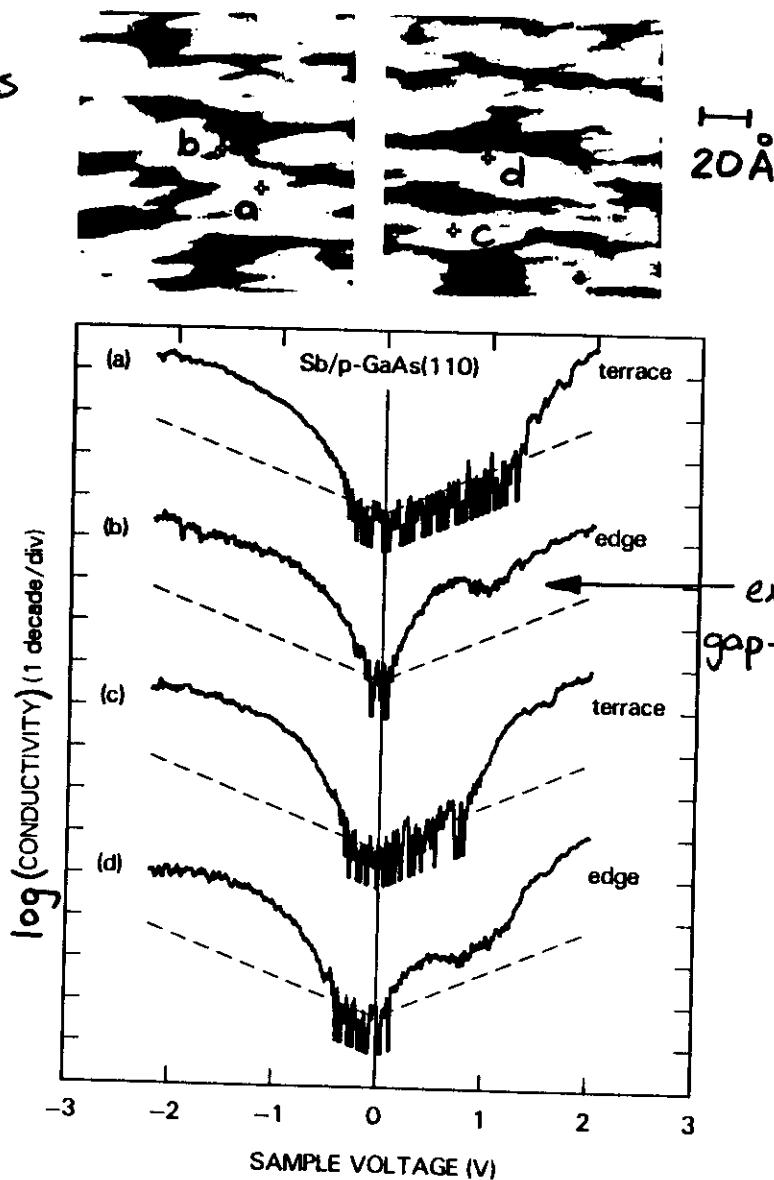
0.25 eV bond-bending on terrace

Photoemission: 0.3 eV on annealed layer
Schäffler, et al. 0.6 eV on unannealed layer
JVST B5, 1048 (1987)



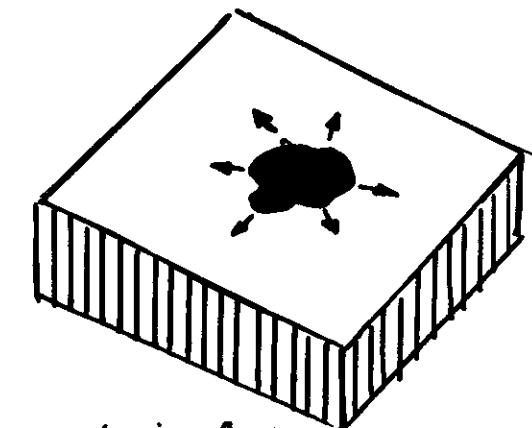
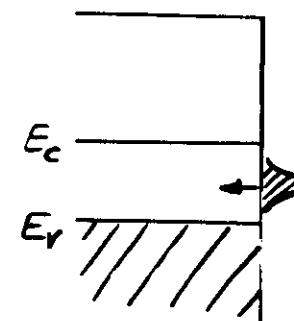
Sb/GaAs

.7 ML



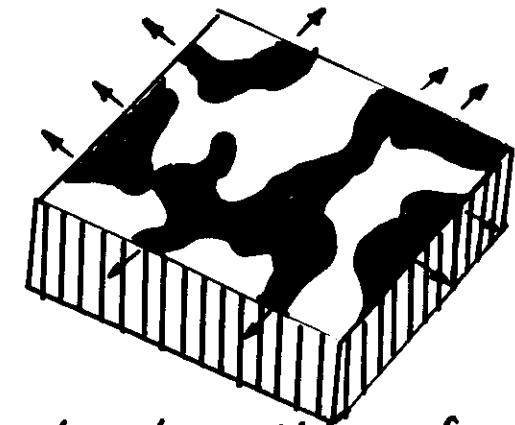
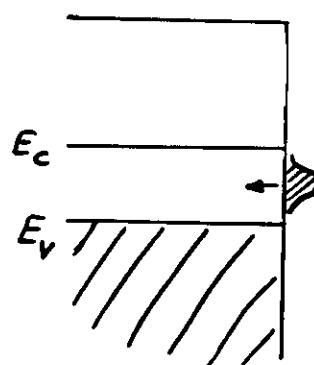
81

Isolated Clusters - Charging Effects



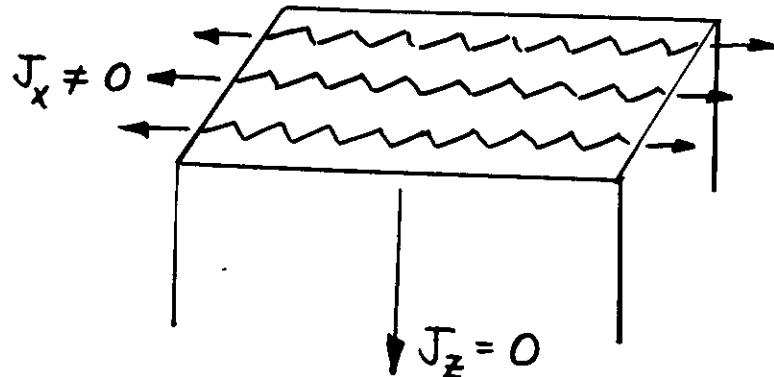
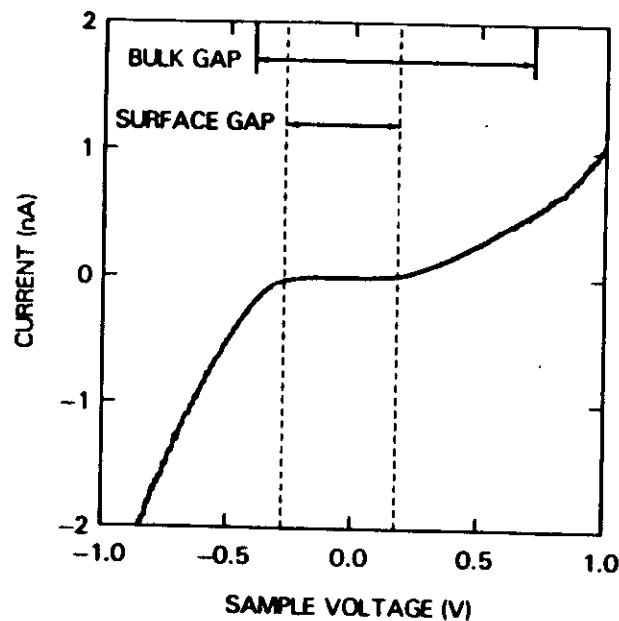
Current cannot propagate in forbidden energy ;

Connected Islands



Current flows only along the surface .

Si(111) 2x1



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Summary

- Geometric Structure,
STM images dangling bonds,
bonds are connected to the surface
atoms.
(only!)
- Surface State Density & Band-bending,
Observed directly in spectroscopy.
(both empty and filled states).
- Charge of Adsorbates and Clusters,
Observed as $\sim 20 \text{ \AA}$ tails in images.
- Current Transport,
Believed to occur along surface.

84

