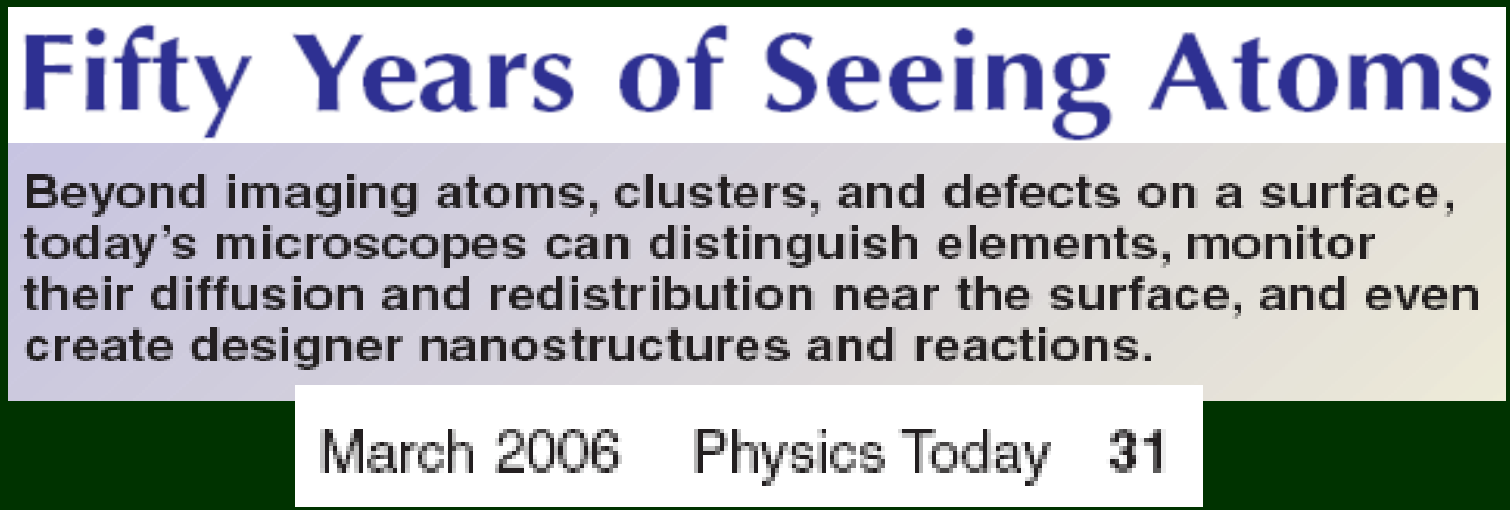
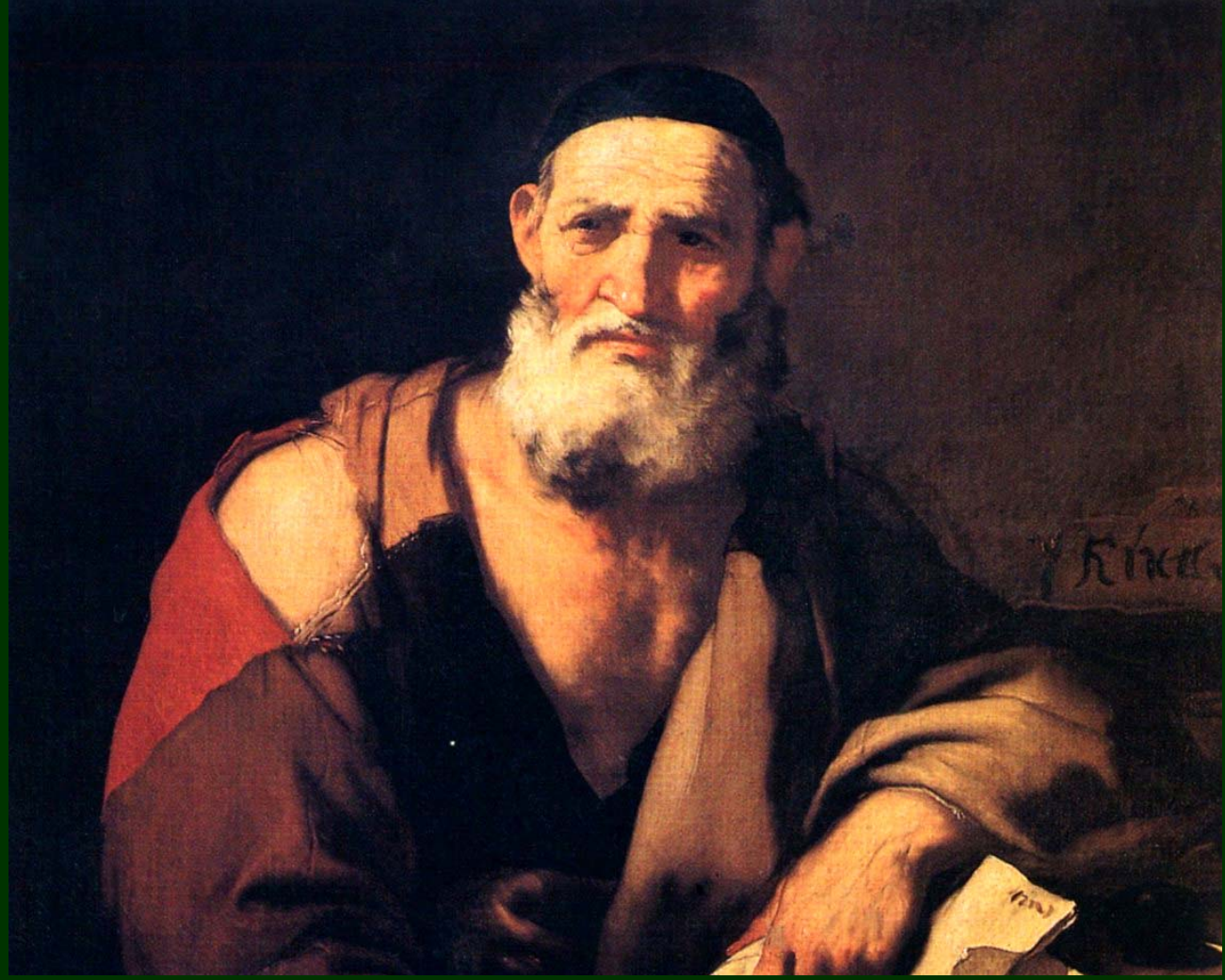
Fifty Years of Seeing and Experimenting with Single Surface Atoms

Tien T. Tsong（鄭天佐）
Institute of Physics, Academia Sinica, Taipei, Taiwan





Democritus (~460 BC)

Leucippus (~5C BC) Epicurus (341-271 BC)

Atoms is the fundamental constituent of matters

A Long Journey to See the Invisible : Atoms

Optical Microscope: 9th c. by Arabs & 15th c. to Europe

Compound Optical Microscope: Z. Janssen in 1590

Galileo in 1609

Seeing microorganisms: van Leeuwenhoek in 1674

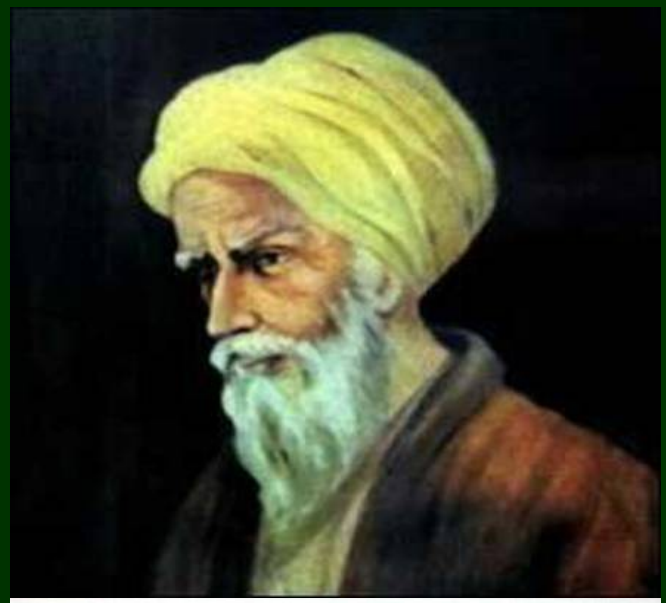
Other important contributors:

Hooke, Huygens

Limitation: lens aberrations, wave diffraction limit

Resolution: $\lambda/2 \sim 3000$ Å

larger than atoms by ~1000



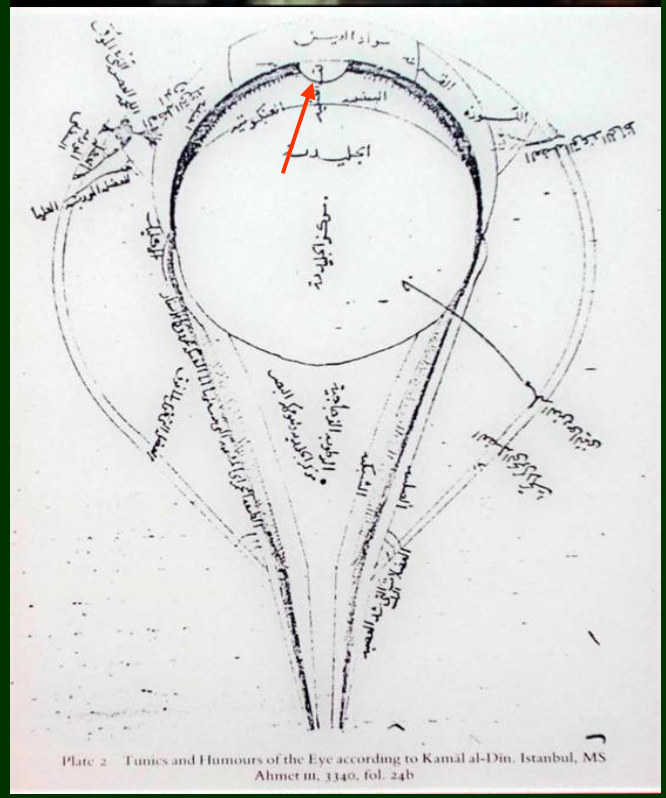


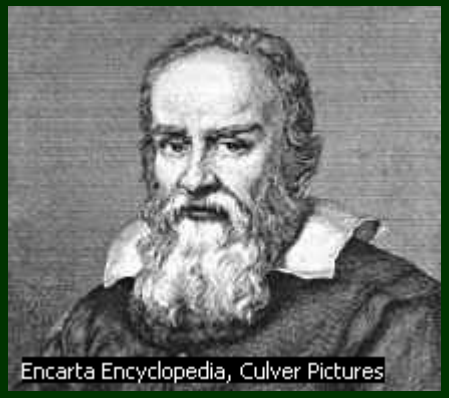
Plate 2 Tunics and Humours of the Eye according to Kamāl al-Dīn. Istanbul, MS Ahmet III, 3340, fol. 24b

Ibn Al-Haytham

(965-c1040) Optics

Detailed analysis of the eye, coupled with light rays entering the eye gave his optics a very modern twist, influenced Kepler and Descartes.

眼睛的構造與光視覺，影響凱普勒和迪卡兒



Galileo

Leeuwenhoek

Huygens

He left no portrait of himself

Hooke

Telescope of Galileo

Compound Optical Microscope of Robert Hooke

Electron Microscope: many recognized the possibility right after de Broglie's matter wave in 1924

Transmission EM: Knoll & Ruska in 1931

Field Emission Microscope: Müller in 1936

Field Ion Microscope: Müller in 1951, atom seen in 1955

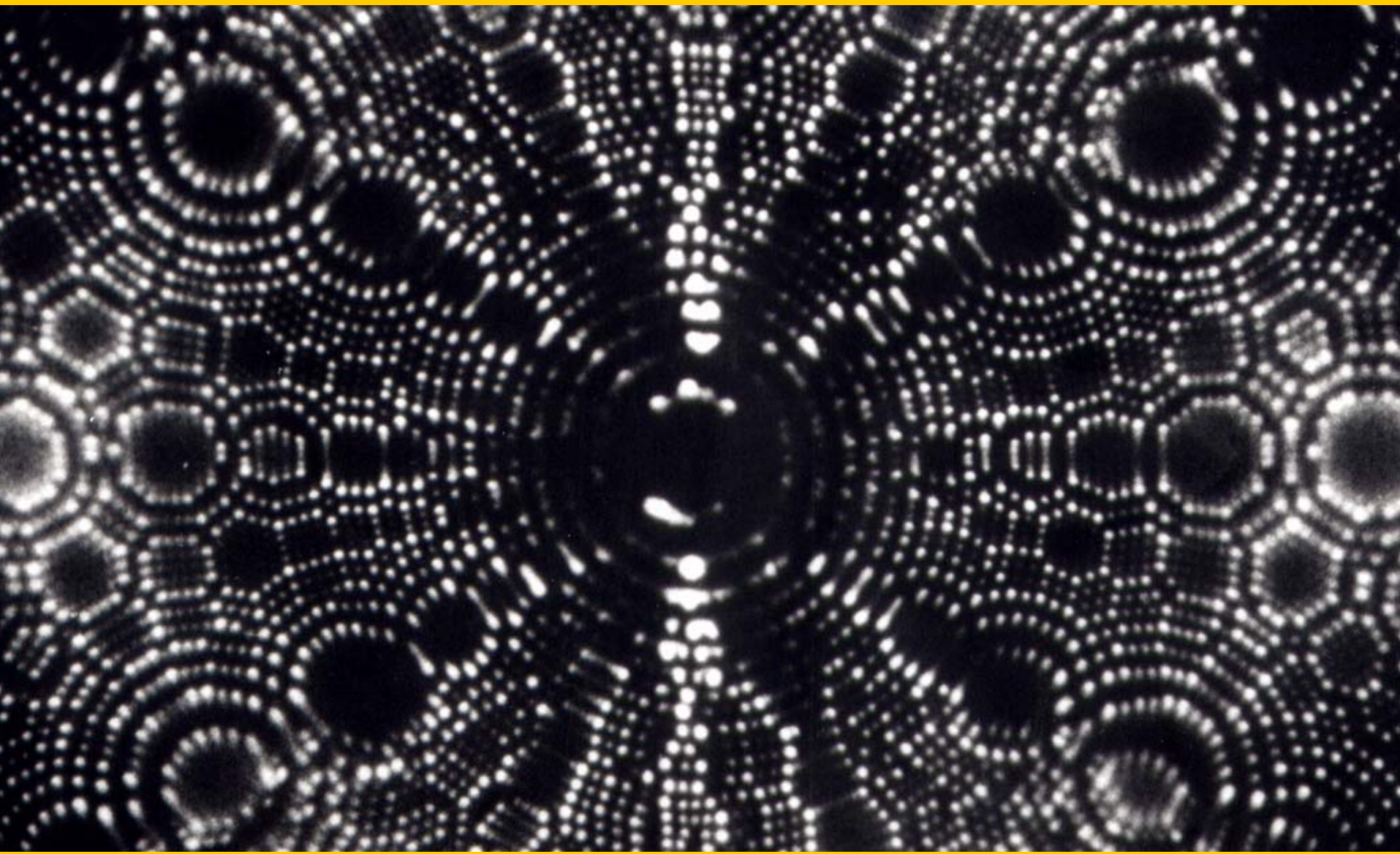
Scanning TEM: high-Z atoms seen in 1969 by Crewe et al.

Topografiner: Young in 1972, scan with three orthogonal piezo pieces, operated in field emission regime

Scanning Tunneling Microscope: Binnig, Rohrer in 1982

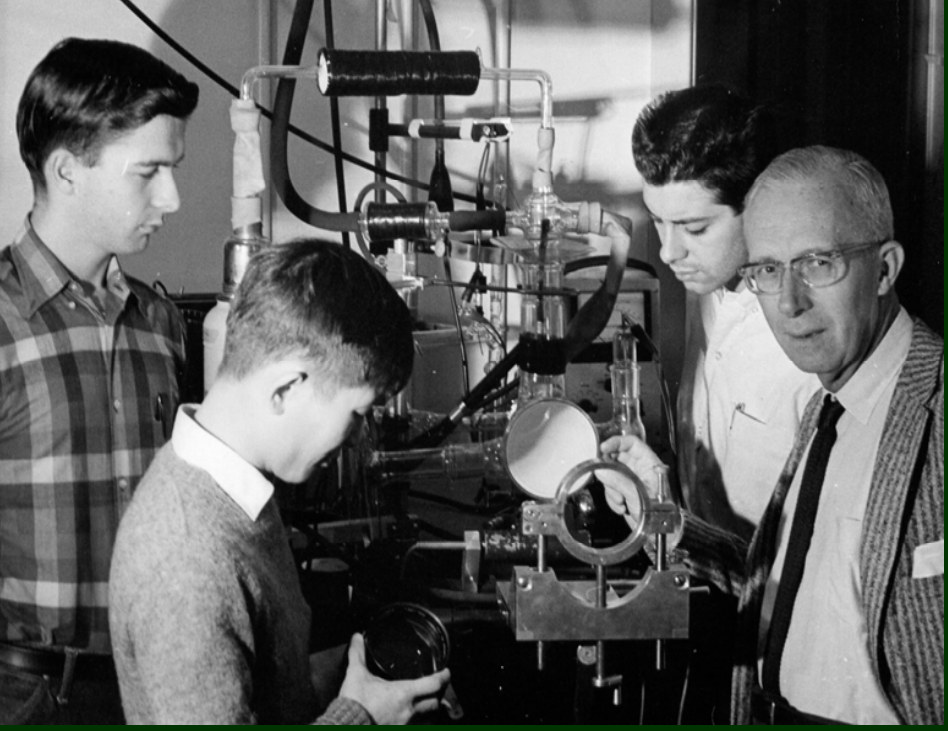
Atomic Force Microscope: Binnig et al. in 1986

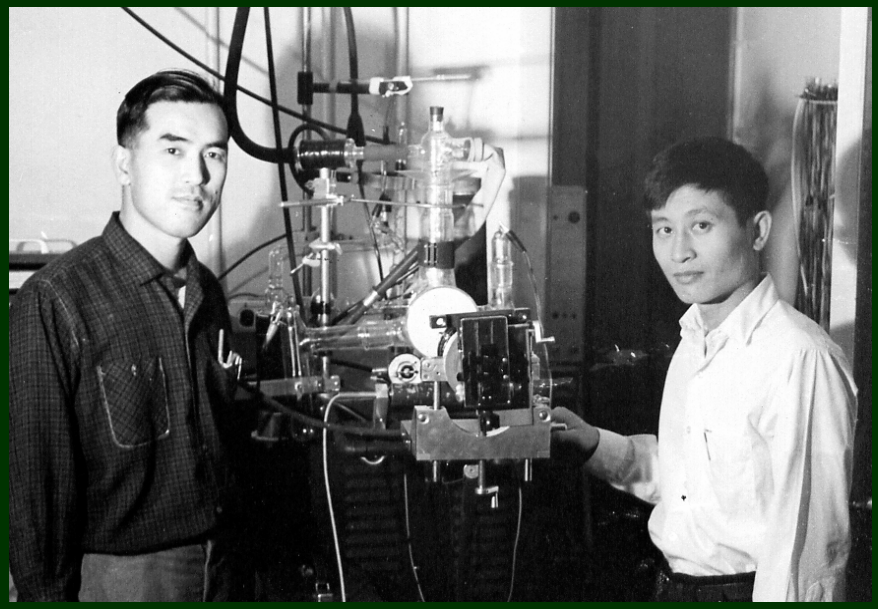
2005: The Golden Anniversary of Seeing Atoms



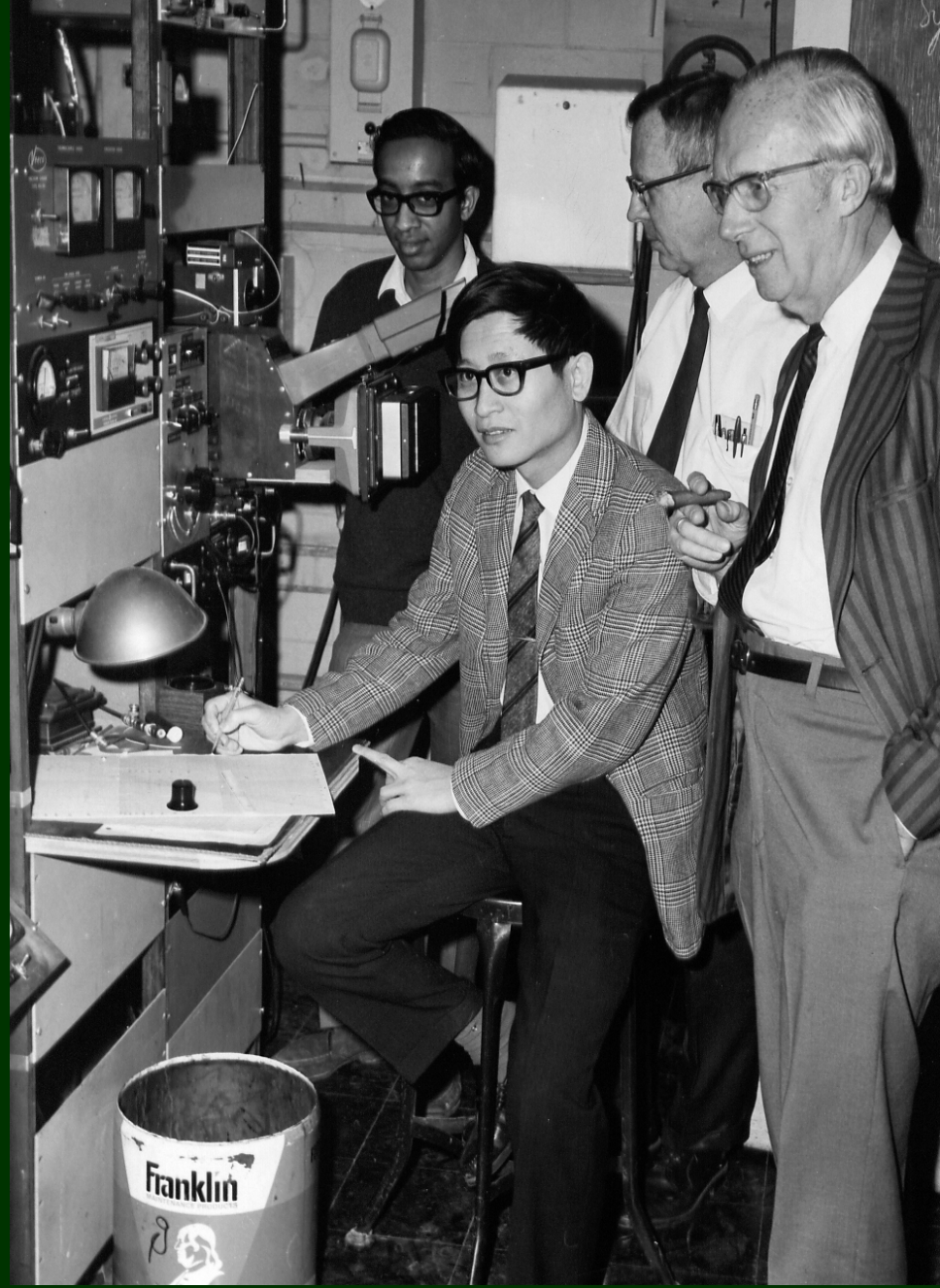
Erwin W. Müller:

Field Emission Microscope 1936, Field Ion Microscope 1951, Atom-Probe FIM 1967

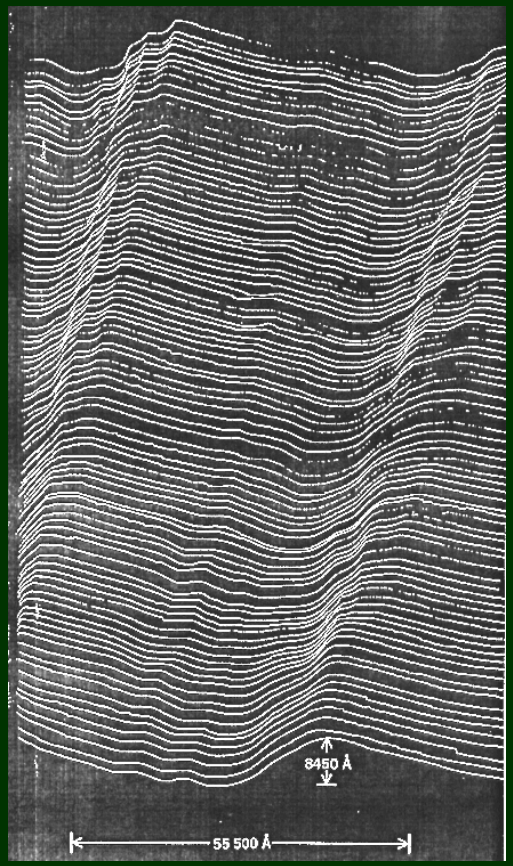




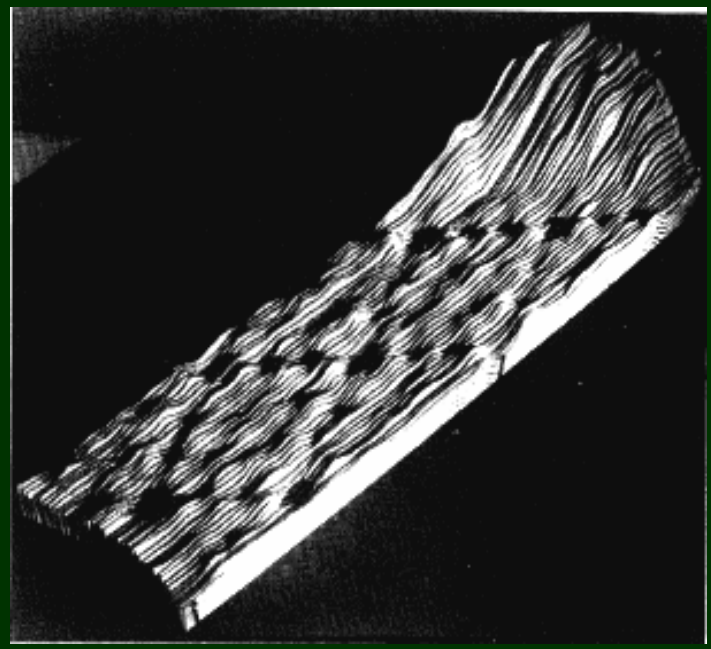
1964



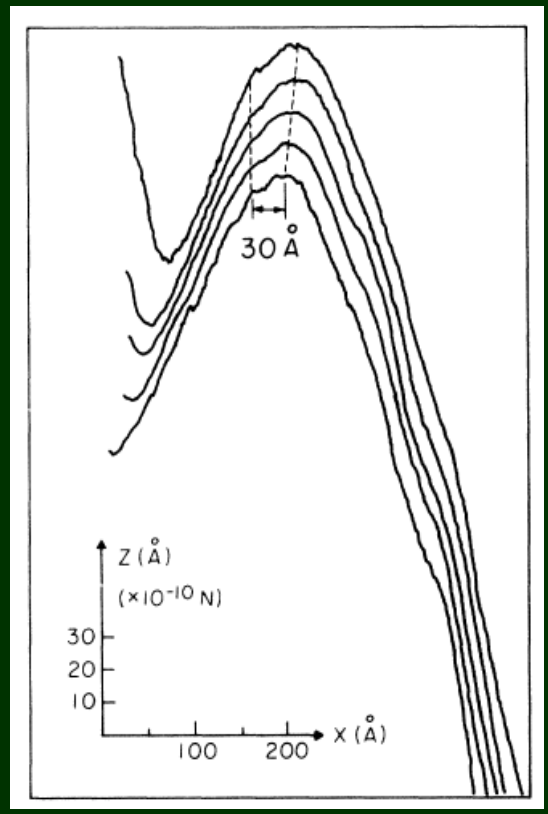
~1972



Topografiner
Young ’71
Field emission mode
Optical Grating



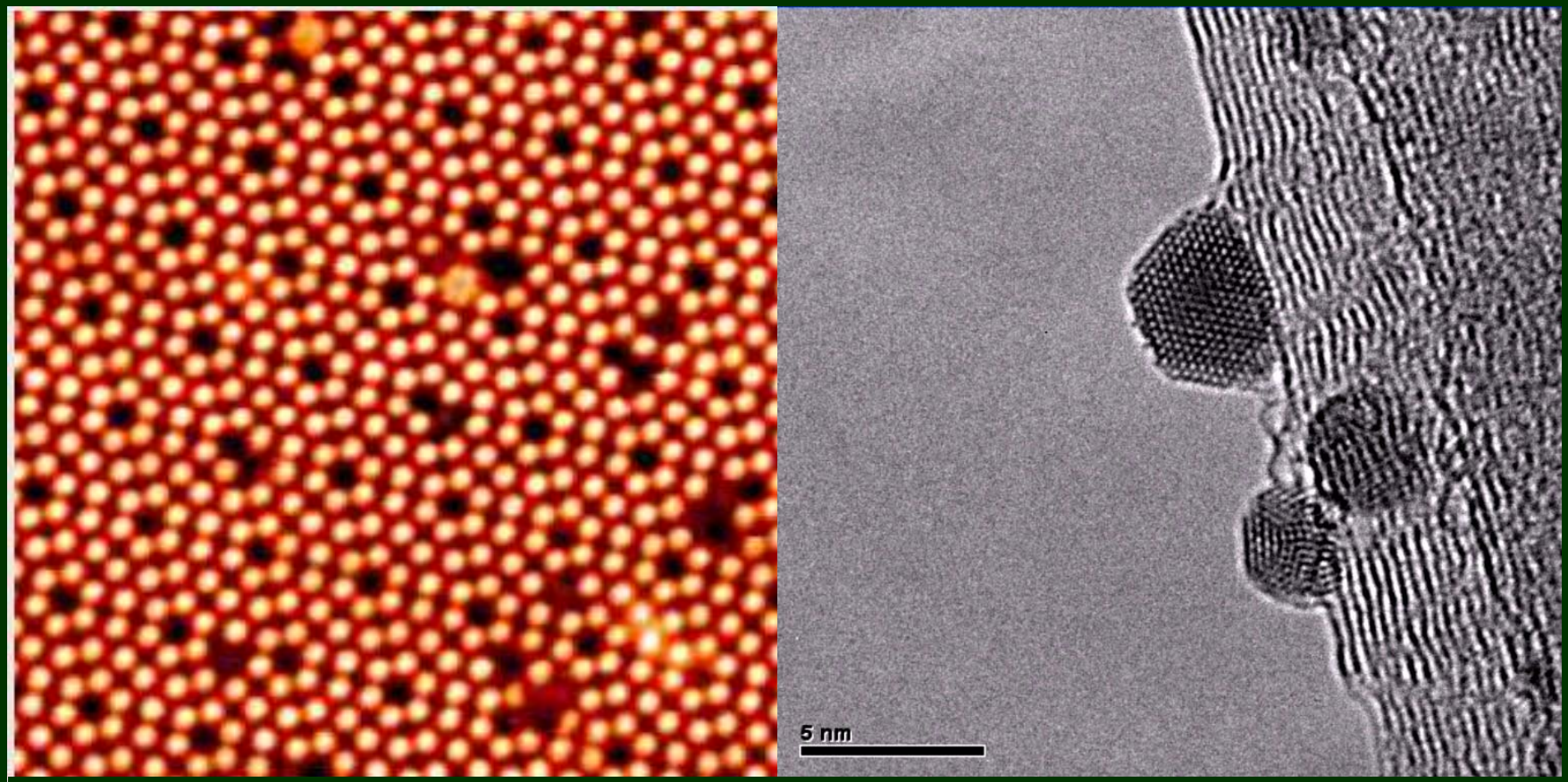
STM
Binnig & Rohrer et al. ’83
Vaccum tunneling mode
Si(111)-7x7 surface



AFM
Binnig et al. ’86
Contact mode
Al_2O_3 ceramic

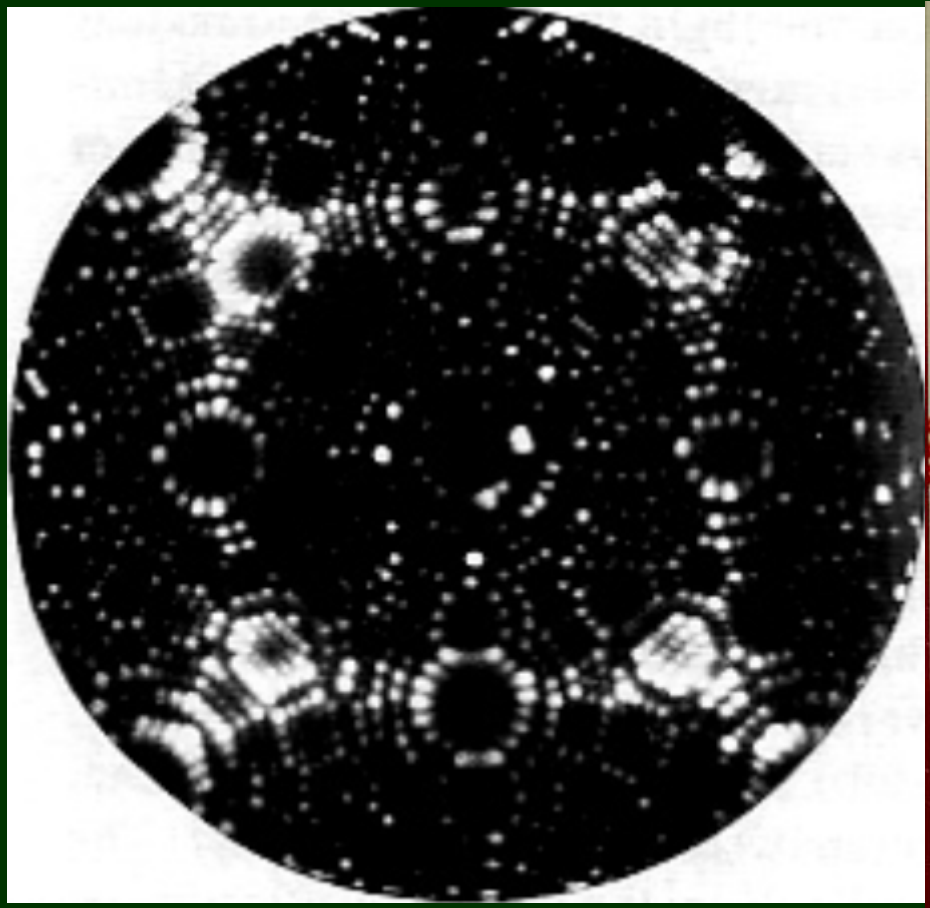
10/15/86 just after the announcement of the Nobel Prize for G. Binnig & H. Rohrer

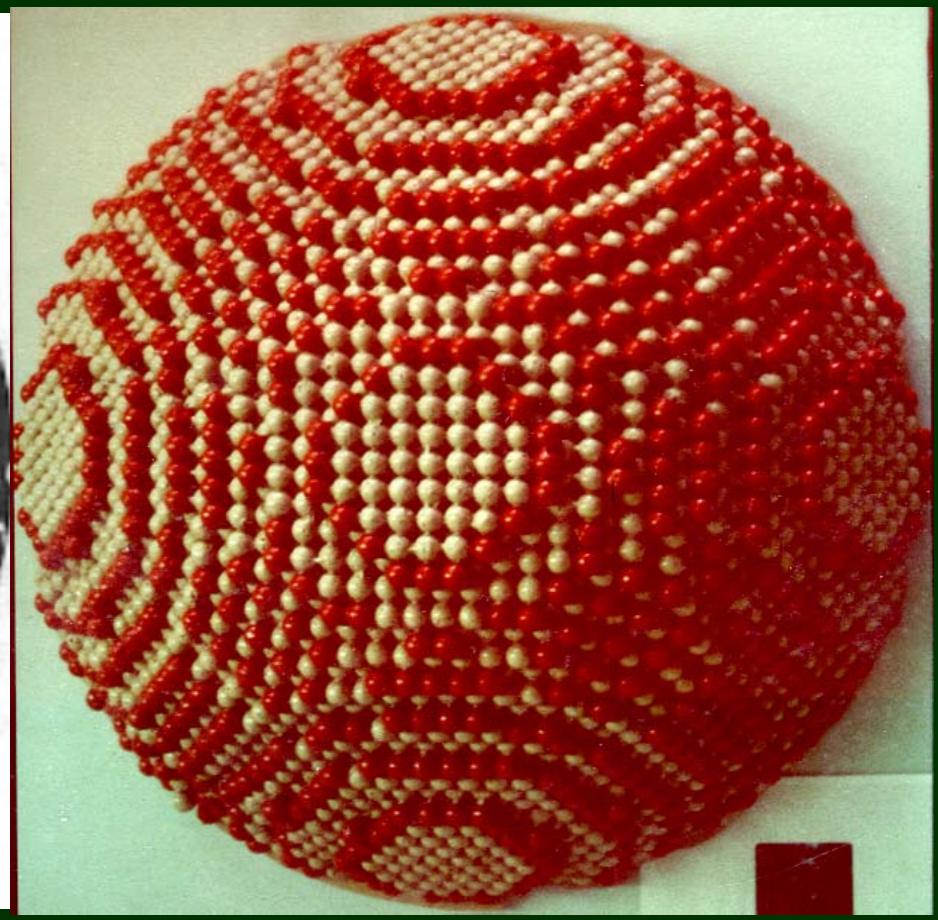
With C. Quate, M. Aono, W. Goodman and K. Sattler in Honolulu, Hawaii in ~2000

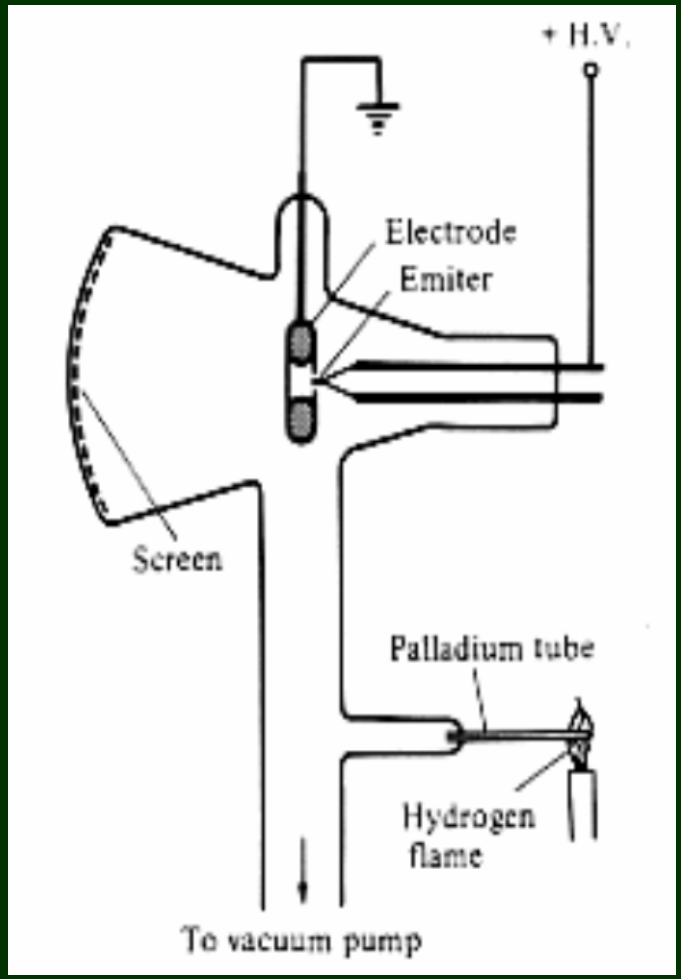


STM & TEM Images of Si(111)-7x7 Surface & Ag Nano Crystals Grown on Multiwall Carbon Nanotube

FIM Image of **Gold** and a Model for an fcc Tip

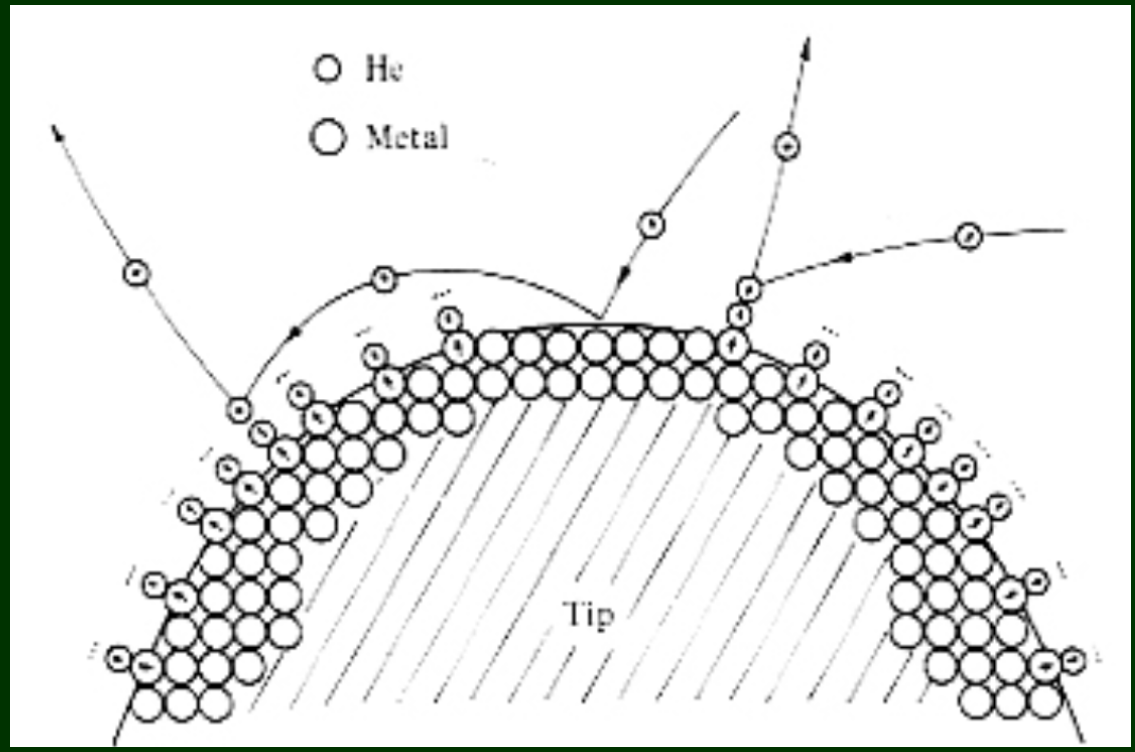






Müller's first FIM (1951)

1960s to early 1970s: Instrumentations & Basic principle



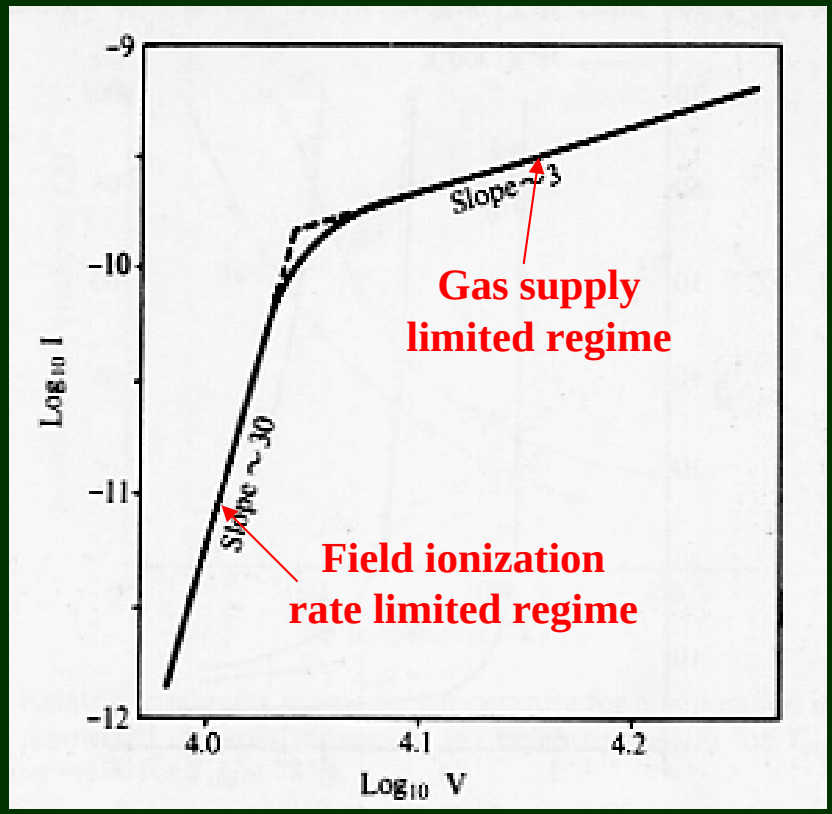
Field evaporation: charge states & rate vs. field

Field adsorption: metal helide ion formation, Langmuir adsorption isotherm

Field ionization: I-V characteristics & ion energy distribution

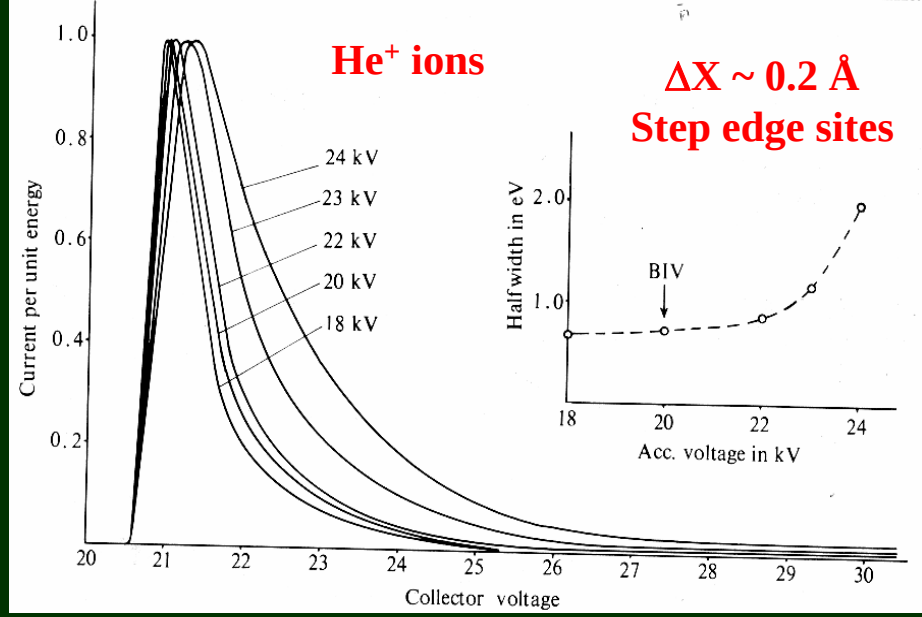
Field Ion Energy Distributions

Field ionization occurs in spatial disks of ~0.2Å

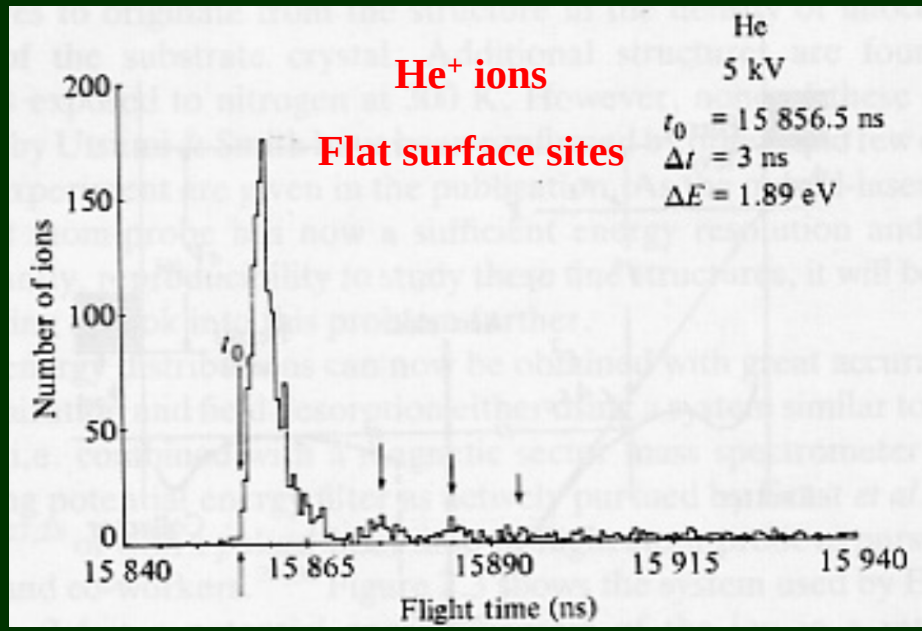


I-V Characteristics

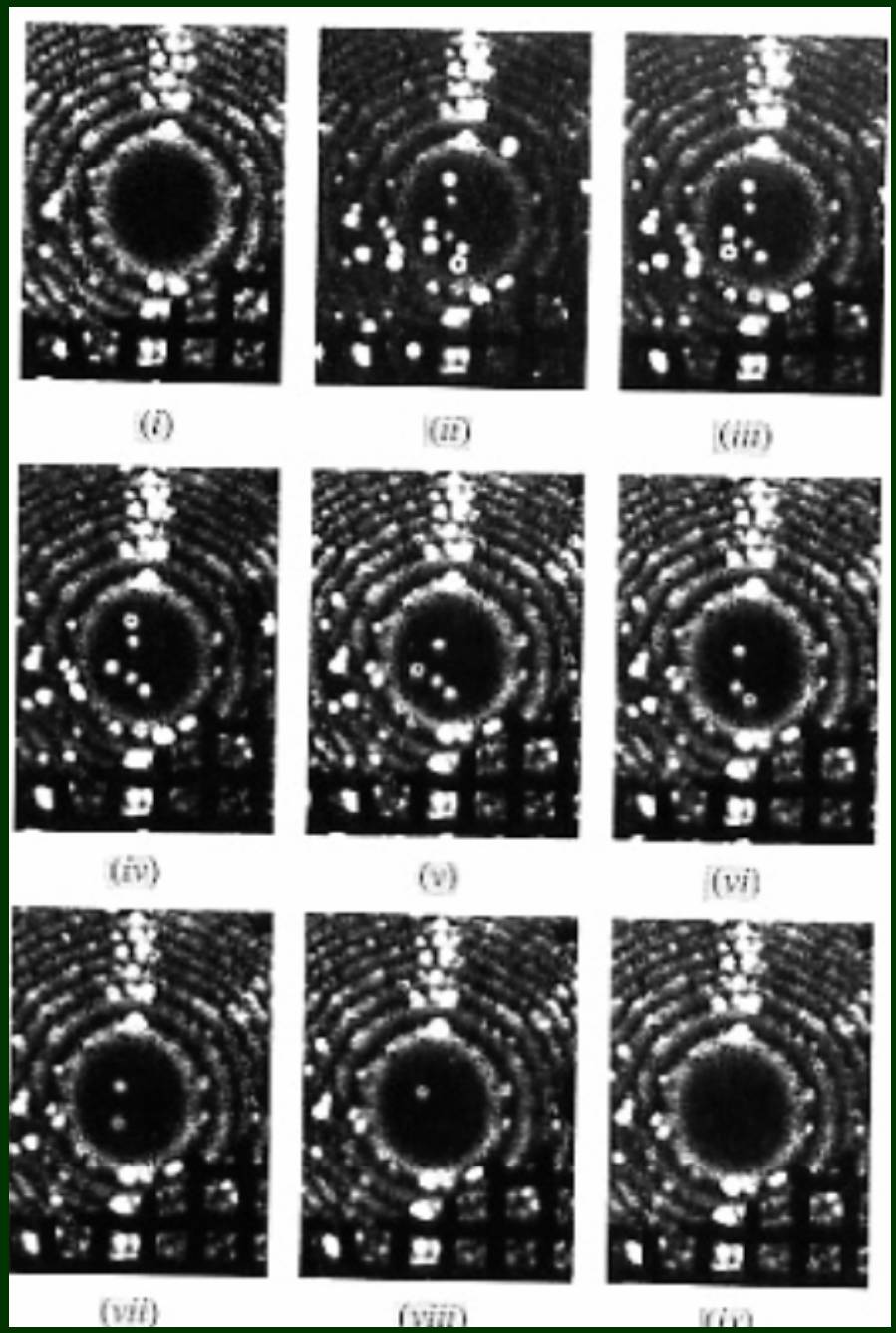
Southon & Brandon, Phil Mag '63



From step edge atoms: Tsong & Müller, JCP '64

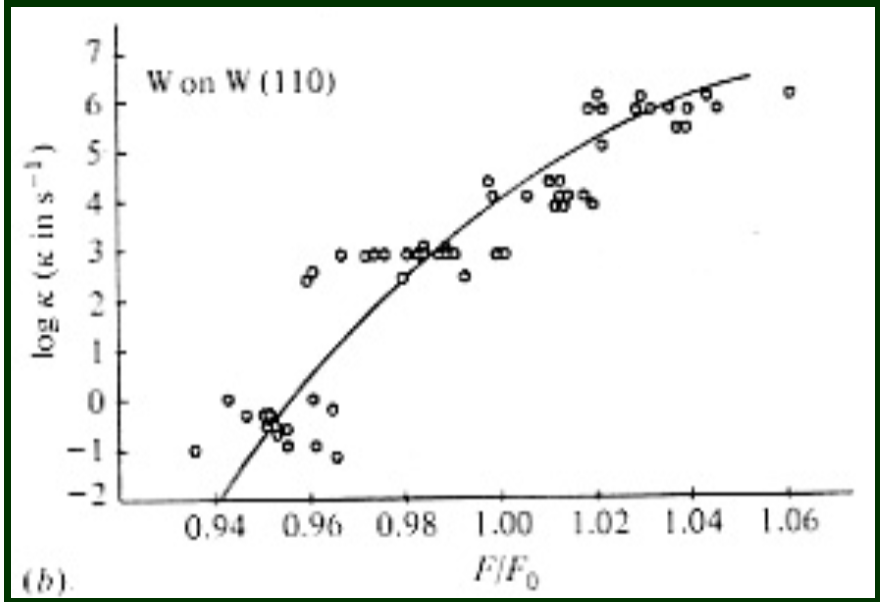


From a flat surface: Jason et al. H^+, H_2^+ & H_3^+ ions, JCP '67



Field evaporation rate vs. Field

Tsong '71



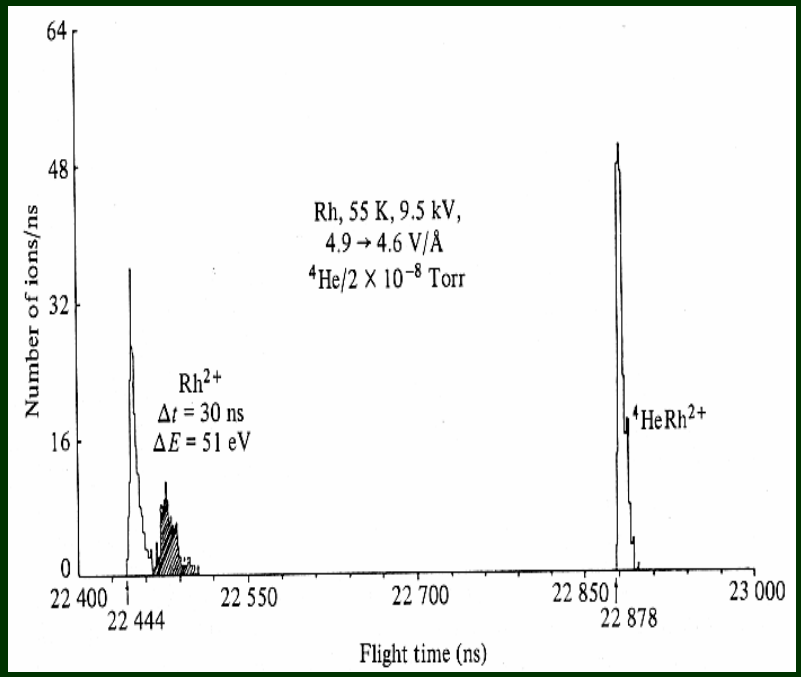
Langmuir Adsorption-Isotherm for Field Adsorption

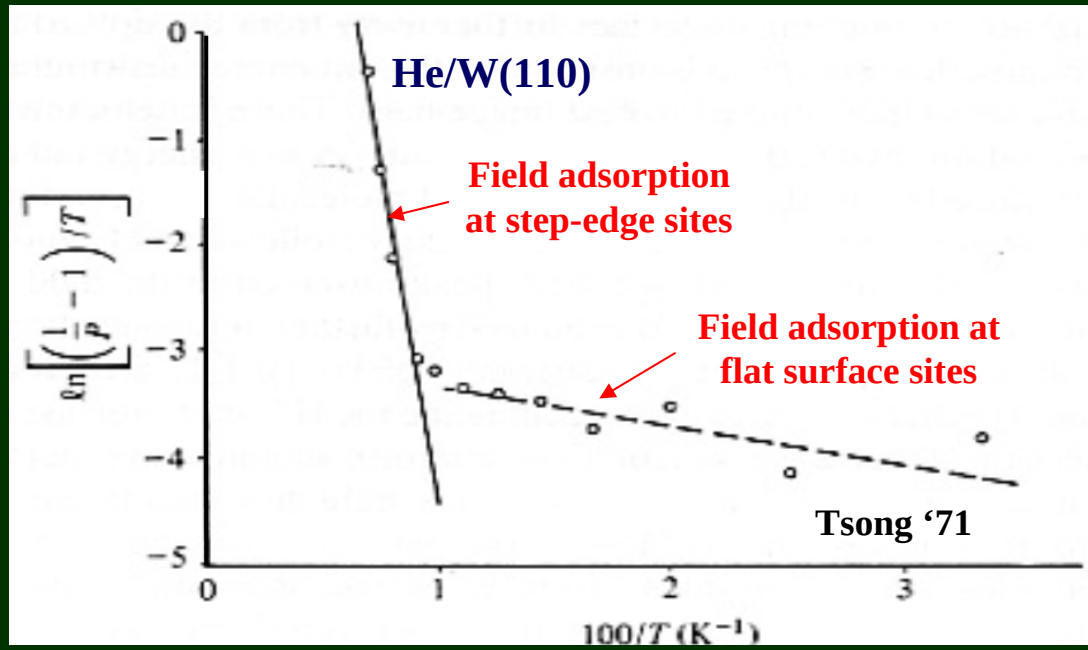
$$p(\infty) = \left[1 + \frac{\nu_0 C T^j}{p_g F_0^i} \exp\left(-\frac{H}{kT}\right)\right]^{-1}. \qquad (2.56)$$

This equation for $i = j = 1$ was originally derived by Tsong & Müller. It was recognized by Rendulic[121] to be a form of Langmuir isotherm specific to field adsorption. The probability of adsorption on a surface atom is of course equivalent to the degree of coverage of the surface if all the atoms in the surface have the same field strength. In the present equation, the field enhancement as well as the time-dependent behavior have been taken into account. For analyzing experimental data, eq. (2.56) is best rearranged in the following form:[115]

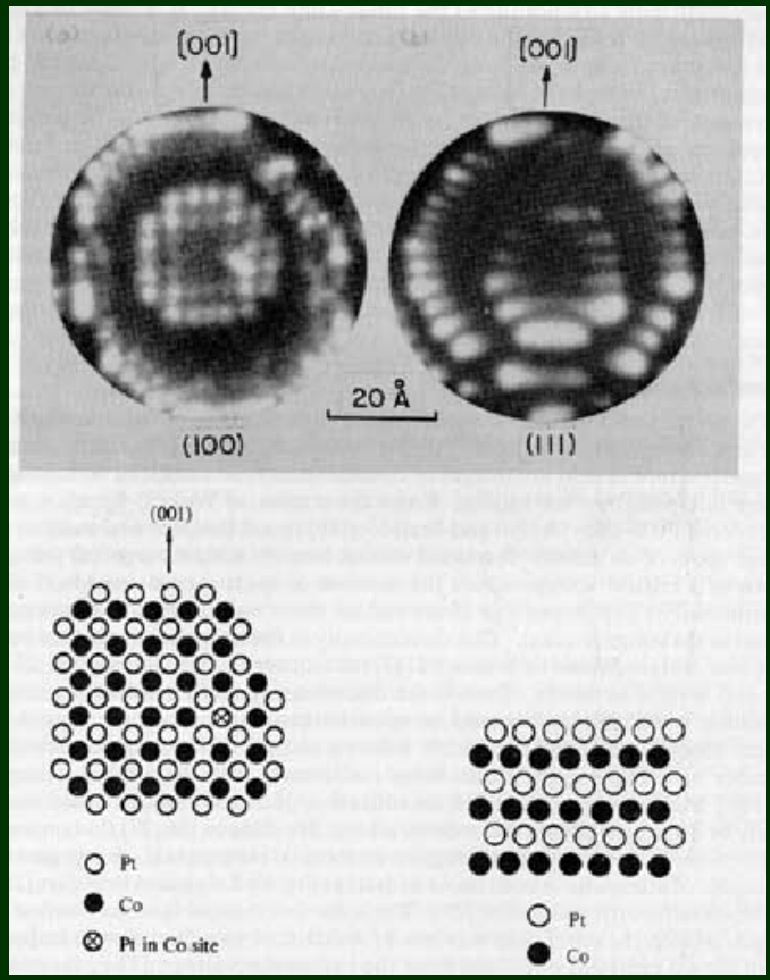
$$\ln\left[\left(\frac{1}{p} - 1\right) \Big/ T^j\right] = \ln\left(\frac{\nu_0 C}{p_g F_0^i}\right) - \frac{H}{kT}. \qquad (2.57)$$

Metal Helide Formation & Field Dissociation





Non-Destructive Chemical Mapping of Surfaces of Ordered Alloys: Images of Ordered Pt_3Co & PtCo



Tsong & Müller, Appl. Phys. Lett. 9 (1966) 7 etc.

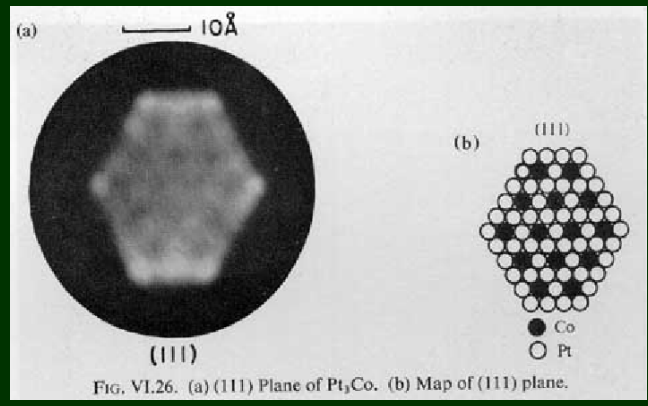
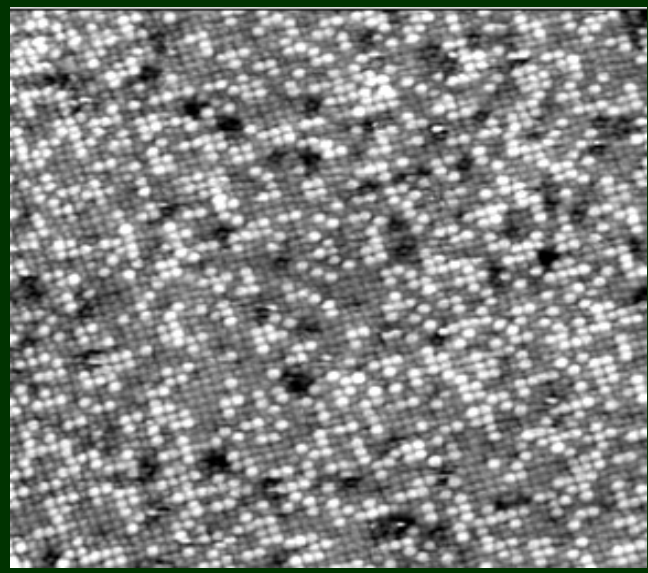


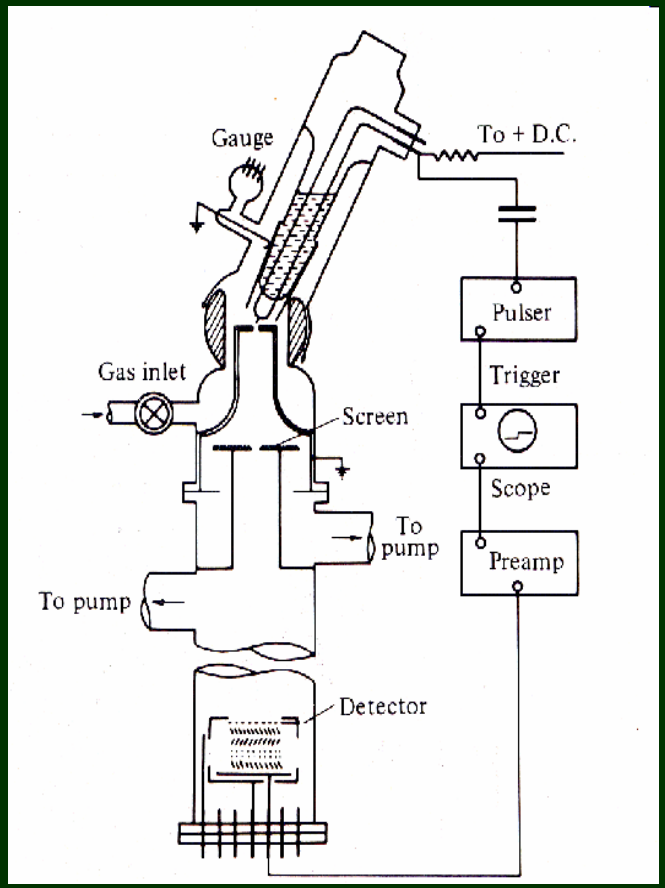
FIG. VI.26. (a) (111) Plane of Pt_3Co. (b) Map of (111) plane.

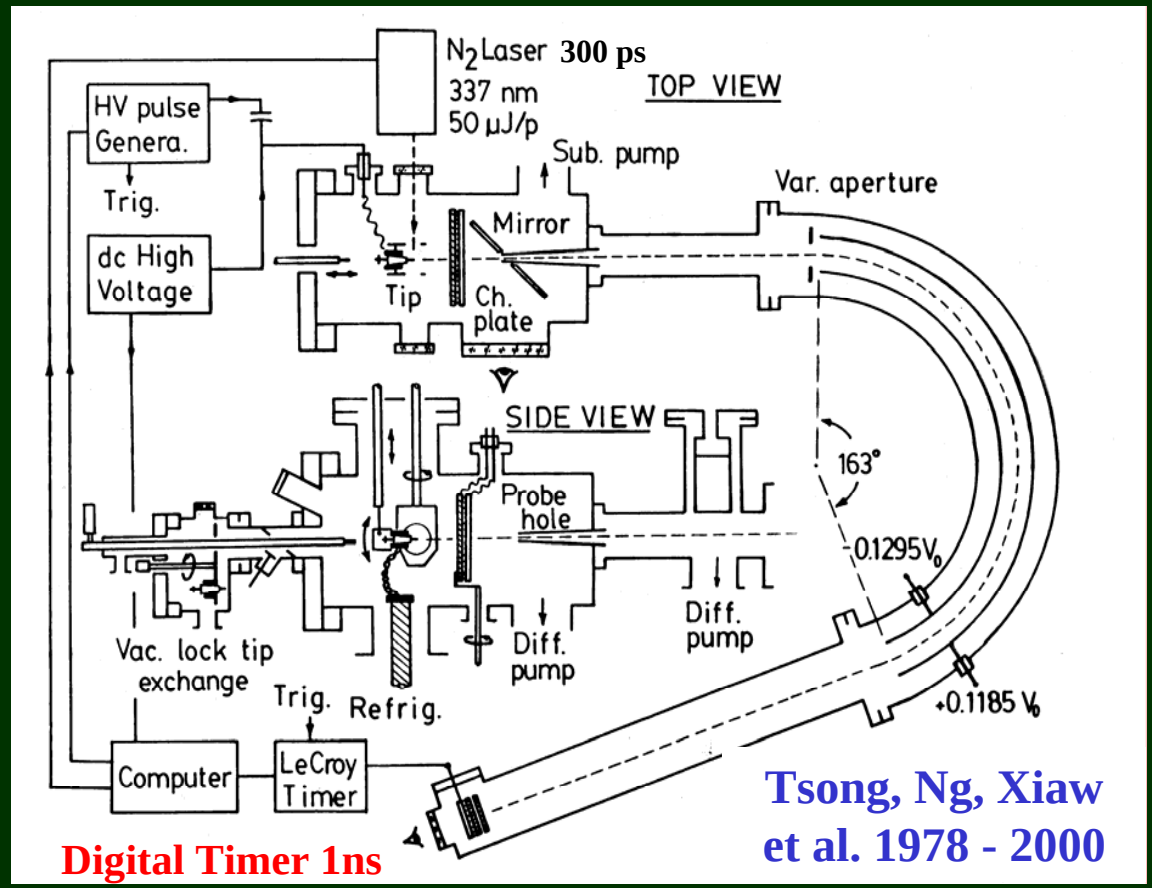


STM image of PtRh
P. Varga et al.

ToF Atom-Probe FIM: flight time focusing method

High voltage pulse operated AP: A very large ion energy spread





Proto type ToF AP

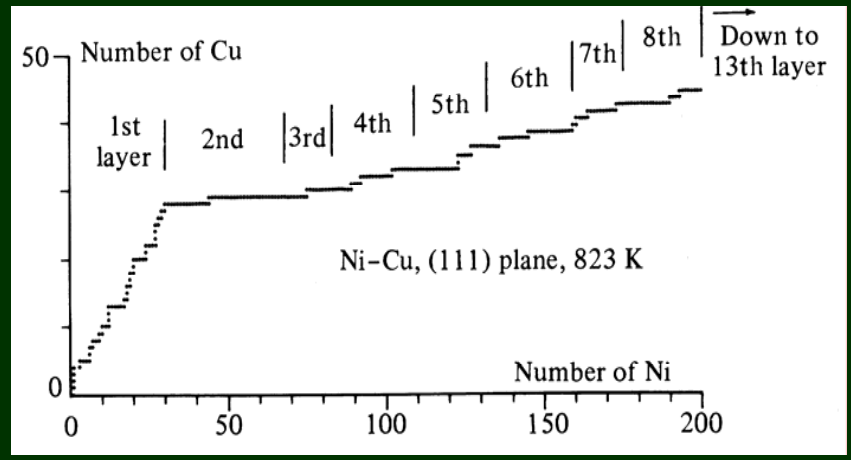
Müller, Panitz & McLane, RSI '68

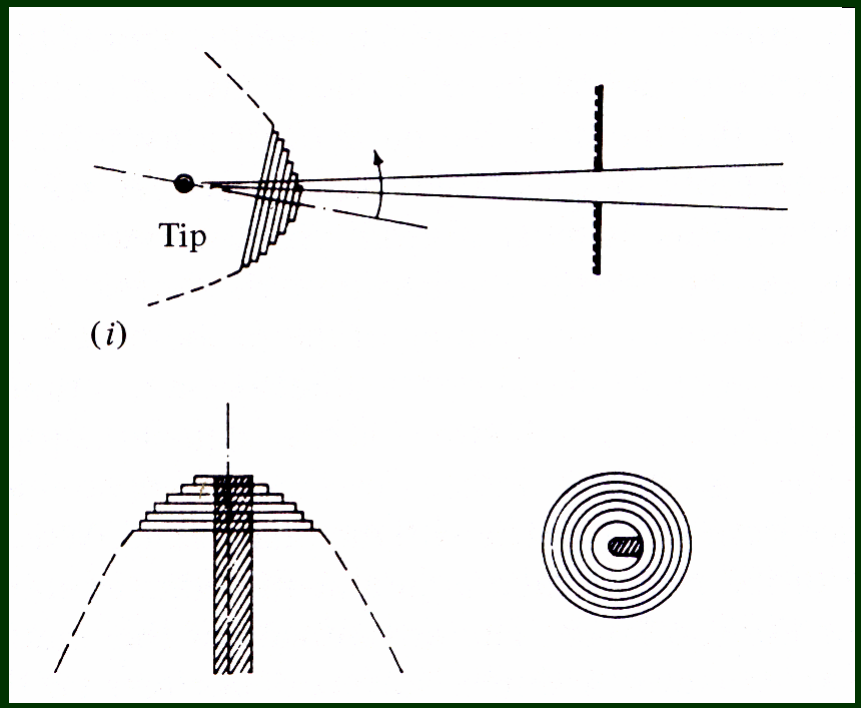
Porschenrieder type ToF AP

Müller & Krisnaswamy, RSI '72

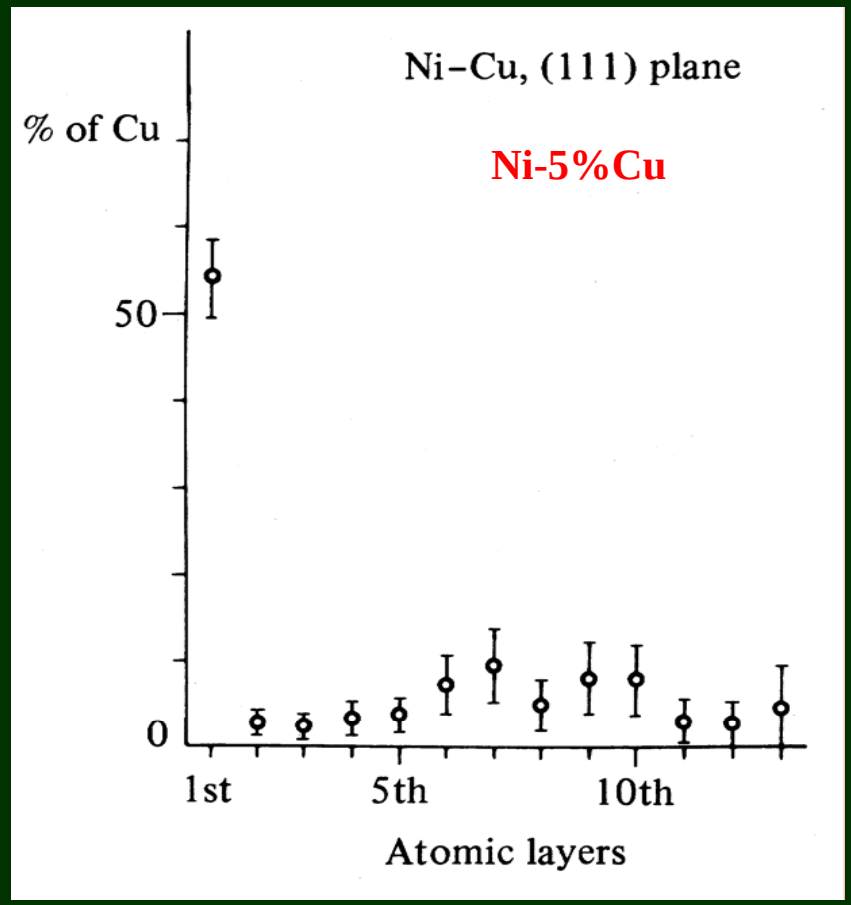
Atomic Layer by Layer
Nano Surface Analysis
in Alloy Segregation

Ni-5%Cu, Ng & Tsong PRL '79



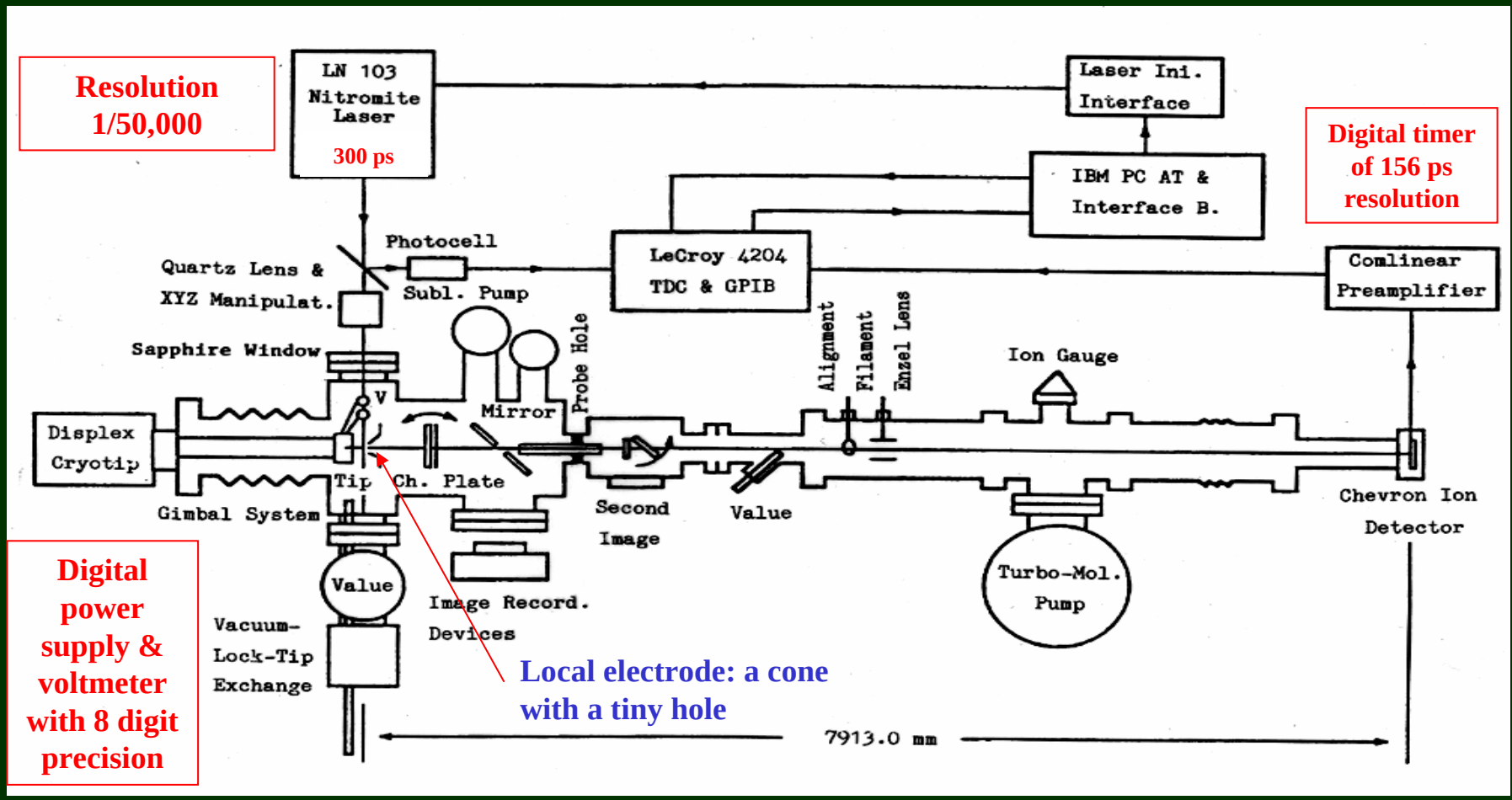


Depth profile & Edge effect



Pulsed Laser Time-of-Flight Atom-Probe FIM (82-90)

Single Atom Chemical & Energy Analysis for Poor Conducting Materials



Local electrode: 1) For reducing the voltage to improve mass resolution. 2) For accurate positioning of the tip. 3) For creating a field free flight path.

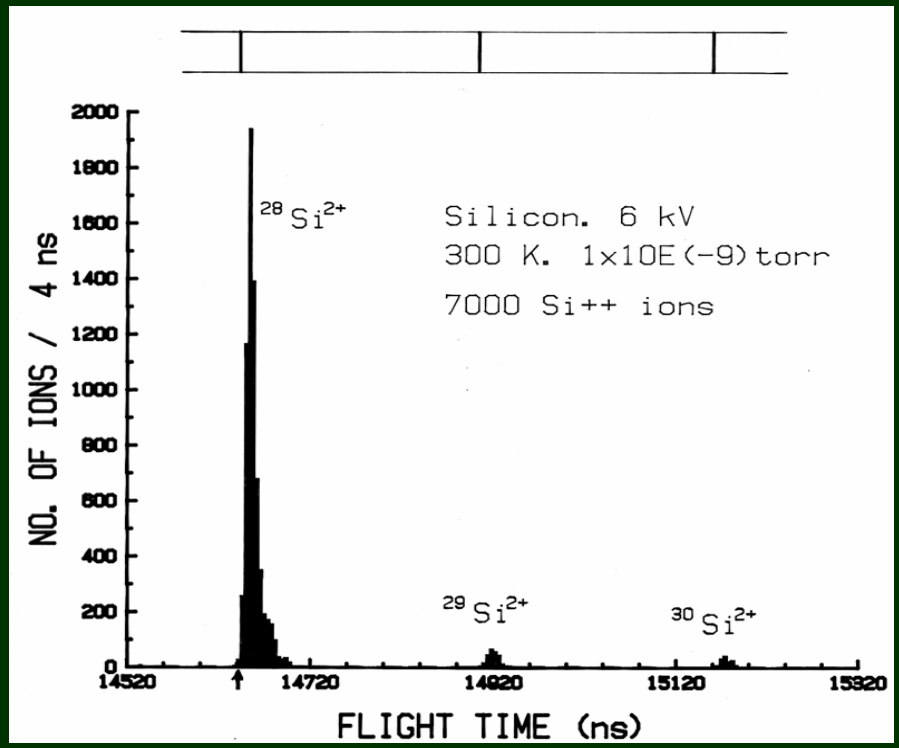
T. T. Tsong, *Atom-Probe Field Ion Microscopy*, Cambridge Univ. Press (90)

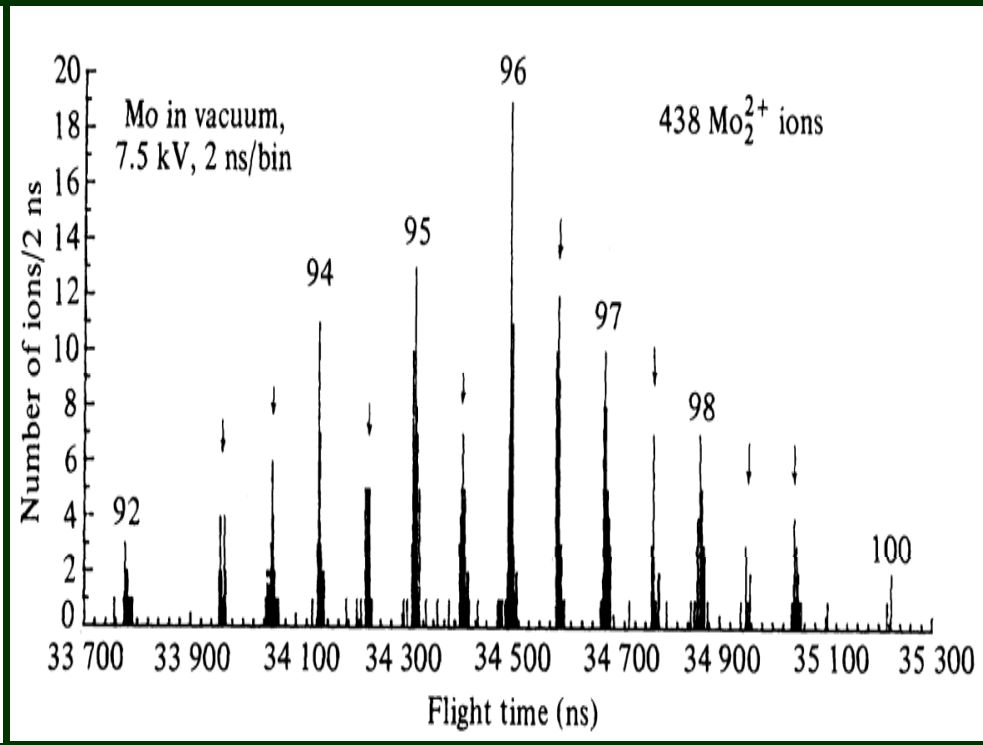
Silicon!

Magic Clusters

No Coulomb Explosion!

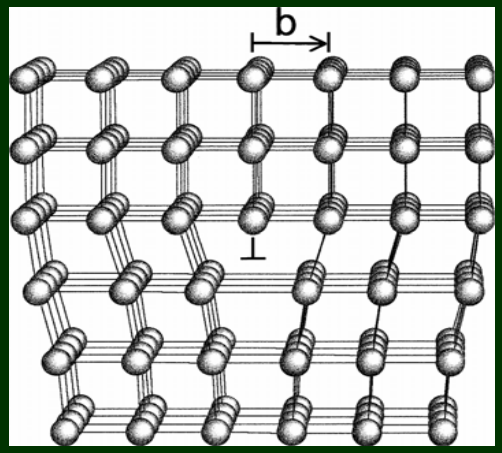
Mo_2^{2+}

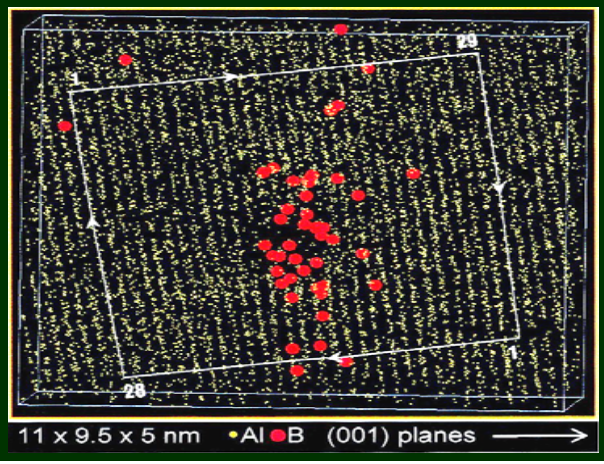




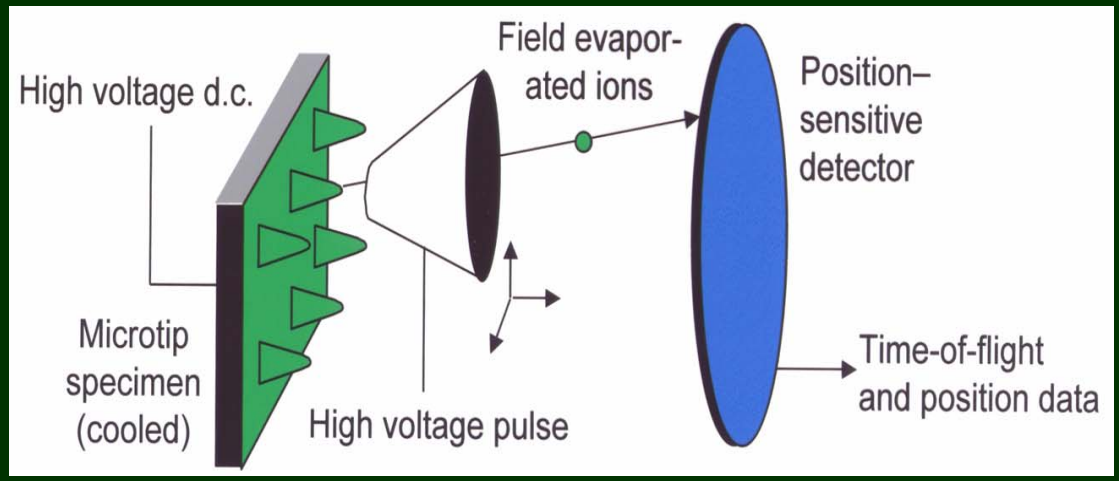
Nano-Analysis with 3D Atom-Probe

Impurity segregation to line dislocation core





Blavette et al.
Science '93



Cerezo & Smith
Oxford Univ.

Kelly et al.: Imago

3D ToF Atom-Probe Field Ion Microscope

Single Atom Experiments:

1. How atoms diffuse and interact on the surface ?

2. How from such interaction atoms grow into a cluster or a nano island and what are their structures ?

3. What are the properties of a surface nano structure ?

Atom & Molecular Dynamics, or Diffusion at Surfaces

Macroscopic Description

Fick's law of diffusion

$$\vec{J} = -\vec{\vec{D}}\nabla c + c(\vec{v})_{\vec{F}}$$

The Question is:

How *D* & <*n*> are related to one another?

Microscopic Description

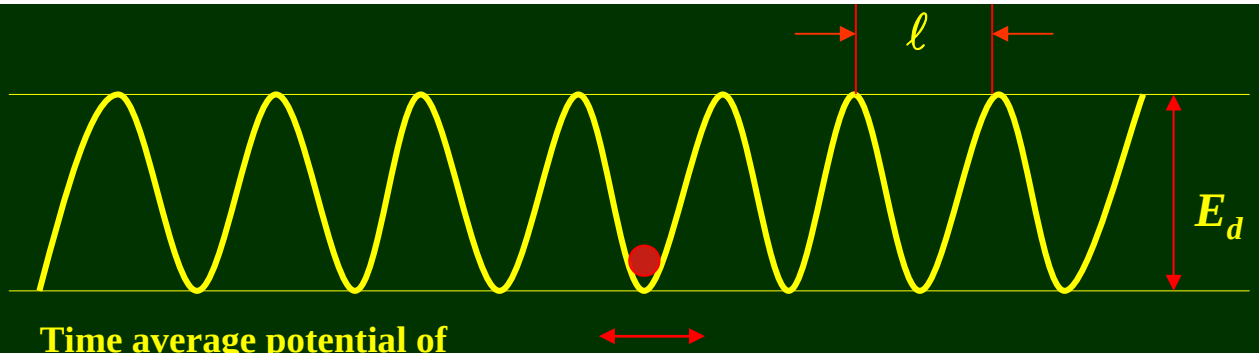
$$U(\vec{r} + \vec{\rho}_n) = U(\vec{r})$$

$\vec{\rho}_n$: Surface lattice vector

$$\bar{n} = \nu_0 \exp(-\Delta G / kT)$$ Average # of jumps/unit time

$$\Delta G = E_d - T\Delta S$$ ΔG: Gibb's free energy ΔS: Entropy

$$\bar{N} = \bar{n}\tau = \tau\nu \exp(-E_d / kT) \quad \text{where} \quad \nu = \nu_0 \exp(\Delta S / k)$$



Time average potential of collective interactions

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 3 1 FEBRUARY 1966

Atomic View of Surface Self-Diffusion: Tungsten on Tungsten*†

GERT EHRLICH AND F. G. HUDDA
General Electric Research and Development Center, Schenectady, New York
(Received 30 August 1965)

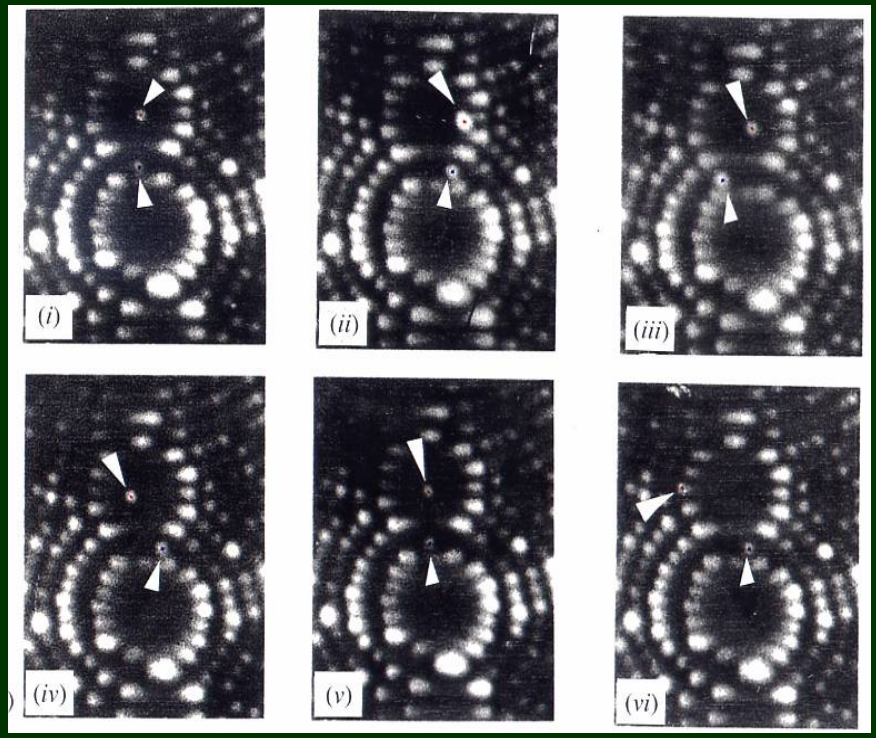
Surface diffusion of tungsten adatoms on several smooth, low-index planes of the tungsten lattice has for the first time been followed by direct observation of individual atoms in the field-ion microscope. Contrary to expectation, the mobility at room temperature is found to increase in the order (211) > (321) ~ (110) > (310) ~ (111). Migrating atoms are reflected at the boundaries of the (110), (211), and (321) planes; on the latter two, motion along atomic rows is favored over diffusion across lattice steps. From quantitative determinations of the rate of change of the mean-square displacement, diffusion coefficients are obtained as follows: (110), $D = 3\times10^{-2}\exp(-22\,000/RT)$ cm²/sec; (321), $1\times10^{-3}\exp(-20\,000/RT)$; (211), $2\times10^{-1}\exp(-13\,000/RT)$. Differences in diffusion on the (211) and (321), planes of very similar structure, suggest a weakening of interatomic forces at lattice edges.

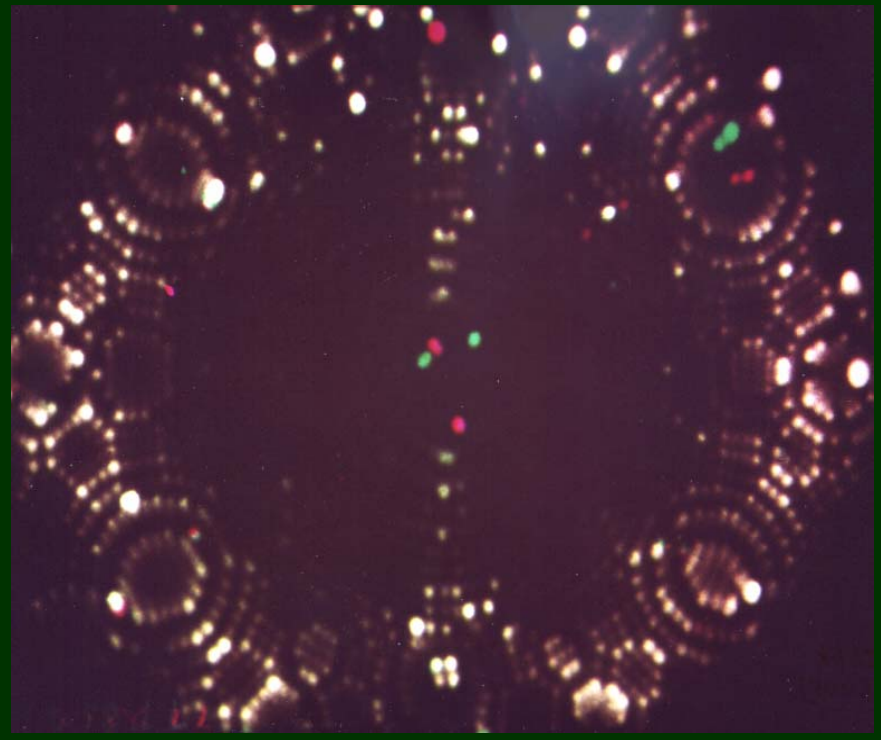
PHYSICAL REVIEW B VOLUME 6, NUMBER 2 15 JULY 1972

Direct Observation of Interactions between Individual Atoms on Tungsten Surfaces*

Tien Tzou Tsong
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 2 February 1972)

Using the field ion microscope (FIM), it is possible to investigate the interactions between individual atoms on metal surfaces. The number of atoms participating in an experiment can be specified and controlled by successive depositions or field evaporations. It is found that the interaction potential between two atoms depends on the substrate surface structure. In agreement with other investigators, the binding energy is found to be not pairwise additive. The interatomic potential between two Re atoms on W (110) planes shows at least two minima and a maximum, suggesting an oscillatory structure similar to the well-known Friedel oscillation. Surface migration as well as structures of clusters with less than six atoms is also investigated. It is found that the equilibrium structures of the clusters depend very sensitively on surface temperature. It is also found that potential traps of ~0.14 eV exist on crystal planes which otherwise appear to be perfectly regular in the FIM images.





Tracing the movements of an atom using FIM

Tsong PRB ‘72

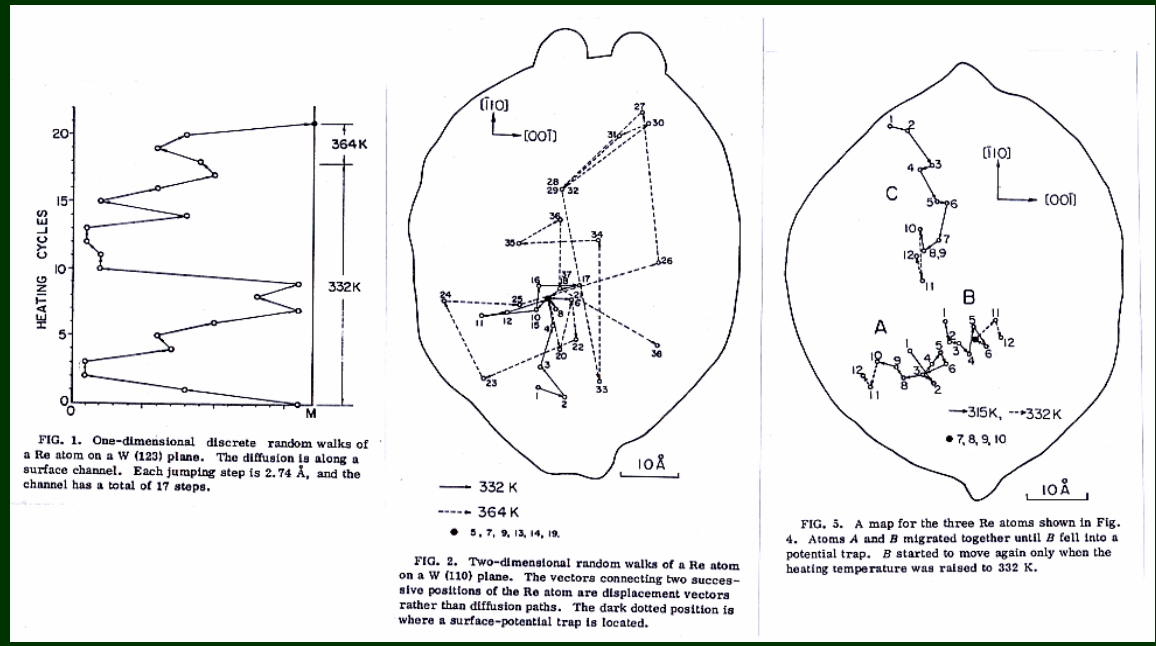


FIG. 1. One-dimensional discrete random walks of a Re atom on a W (123) plane. The diffusion is along a surface channel. Each jumping step is 2.74 Å, and the channel has a total of 17 steps.

FIG. 2. Two-dimensional random walks of a Re atom on a W (110) plane. The vectors connecting two successive positions of the Re atom are displacement vectors rather than diffusion paths. The dark dotted position is where a surface-potential trap is located.

FIG. 3. A map for the three Re atoms shown in Fig. 4. Atoms *A* and *B* migrated together until *B* fell into a potential trap. *B* started to move again only when the heating temperature was raised to 332 K.

Commemoration of the 100th Anniversary of Einstein's Miraculous Year 1905

Einstein Relation in Random Walk

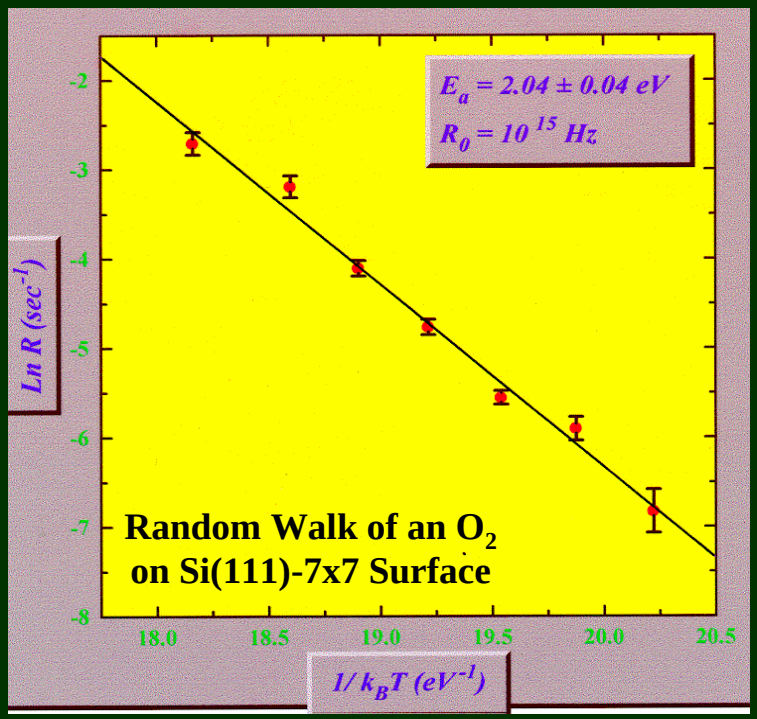
$$D_S = \frac{\langle (\Delta r)^2 \rangle}{2m\tau} = D_0 \exp\left(-\frac{E_d}{kT}\right)$$

$$\because \langle (\Delta r)^2 \rangle = \overline{N}\ell^2 = \overline{n}\,\tau\ell^2 = \nu_0 \tau \ell^2 \exp\left(-\frac{E_d}{kT}\right)$$

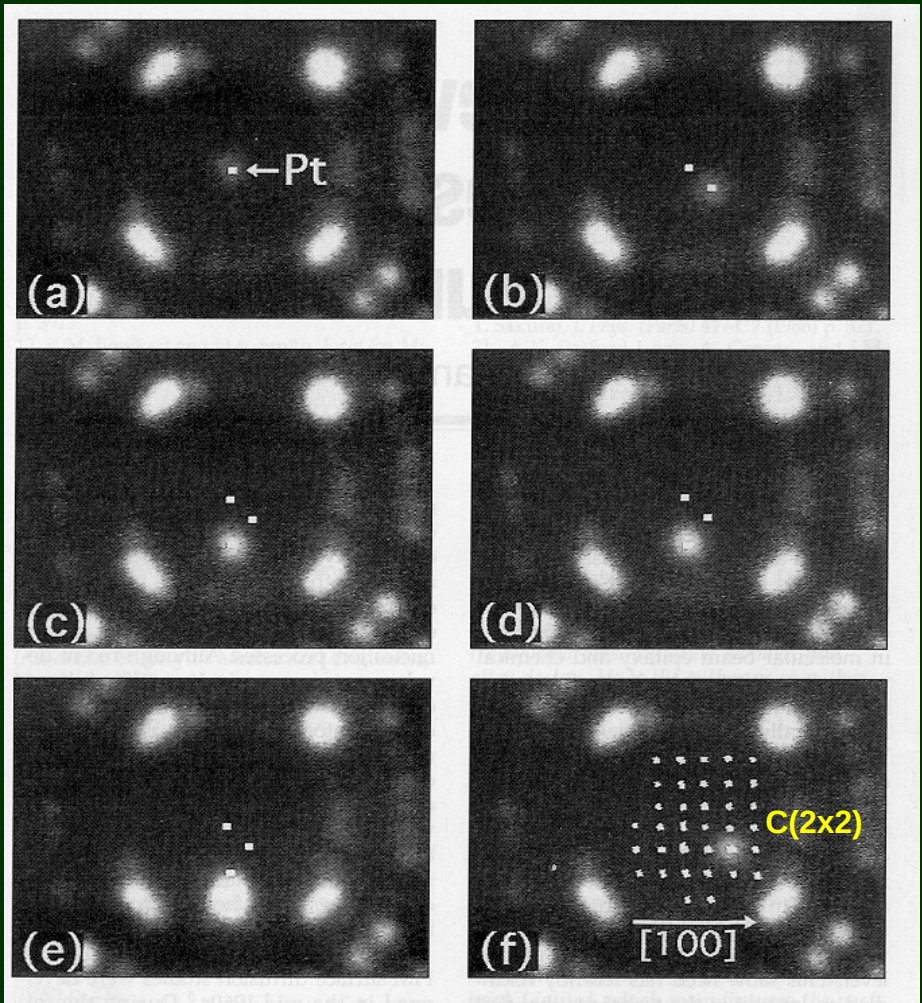
$$\therefore D_0 = \frac{\nu_0 \ell^2}{2m}$$ **Diffusivity**

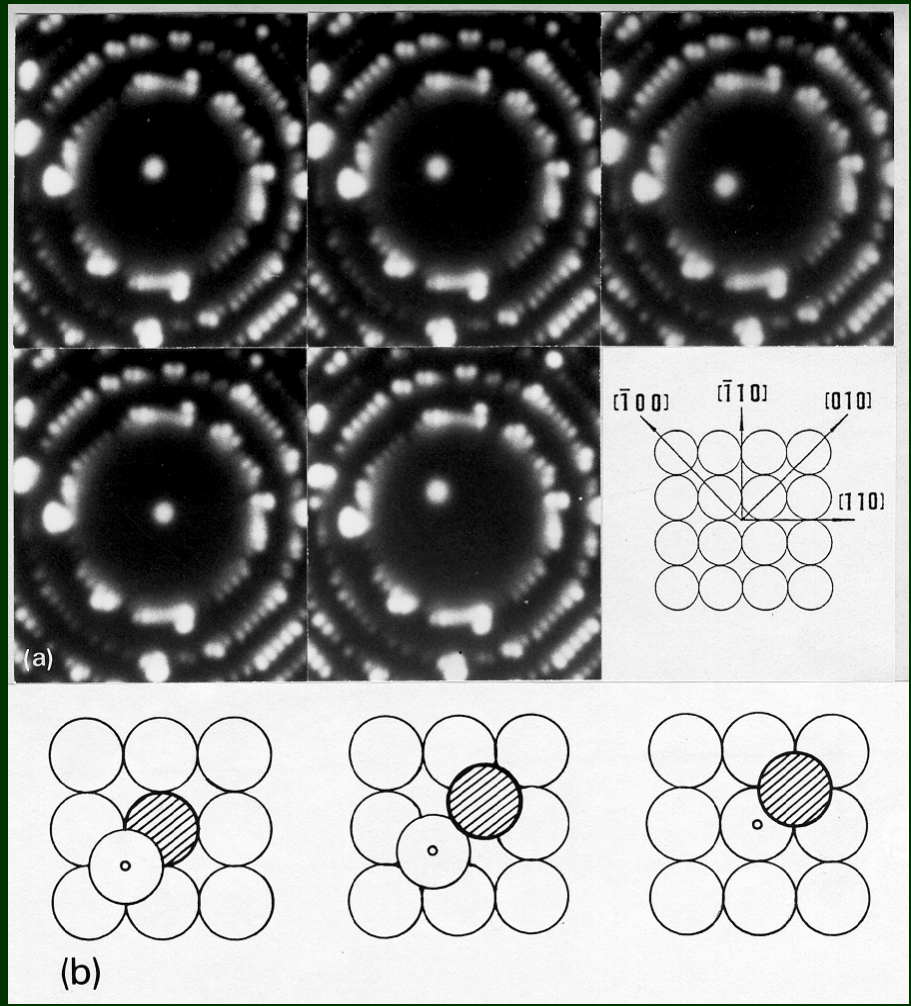
$$\overline{n} = R = \frac{\langle (\Delta r)^2 \rangle}{\tau\ell^2} = \nu_0 \exp\left(-\frac{E_d}{kT}\right)$$

$$\ell n(R) = \ell n\left(\frac{\langle (\Delta r)^2 \rangle}{\tau\ell^2}\right) = \ell n(\nu_0) - \frac{E_d}{kT}$$ **Arrhenius-Einstein plot**



Atomic-Exchange diffusion mechanism: Ir/Ir(001)



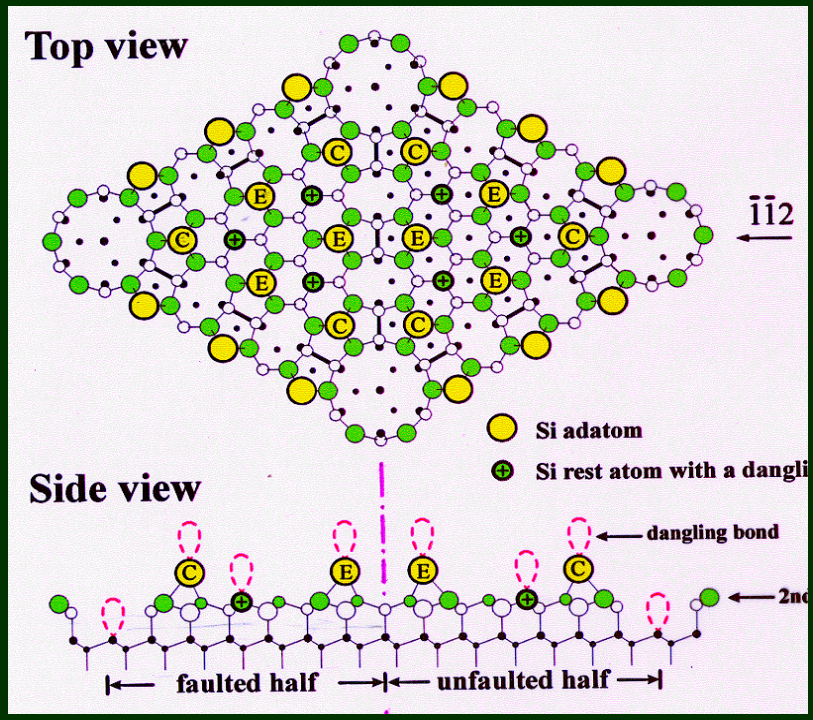


Tracking the movement of one surface atom

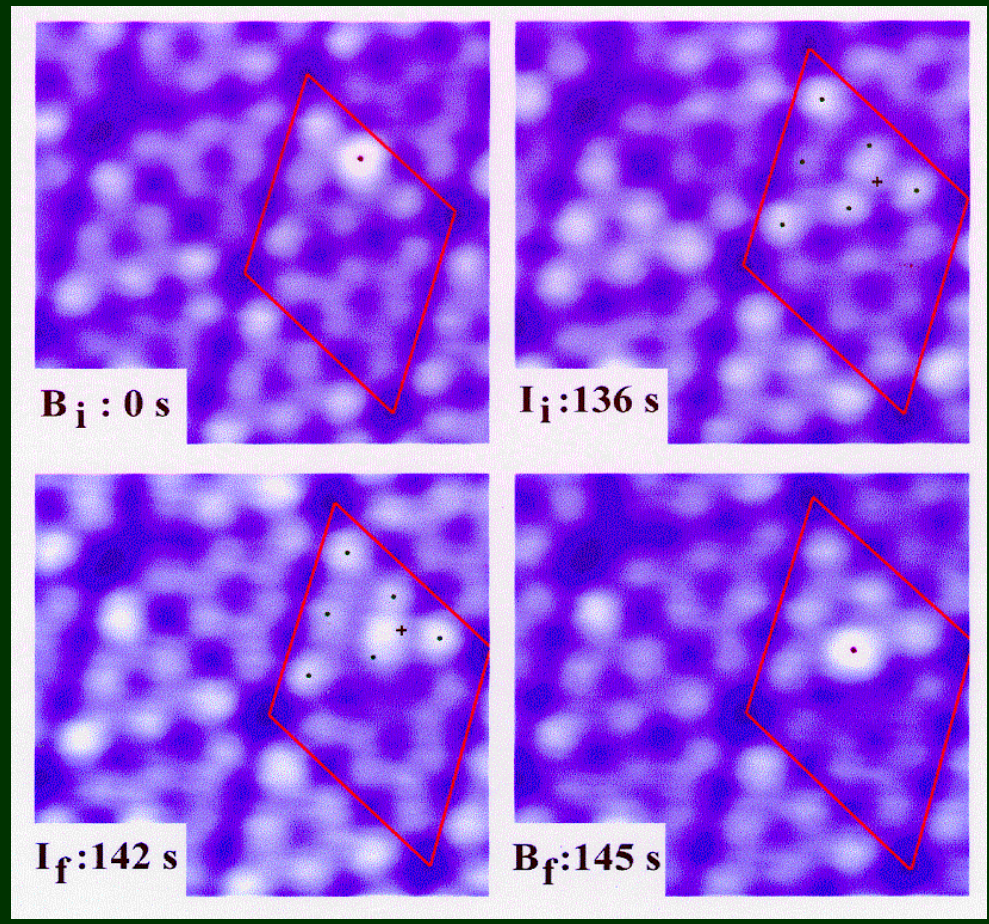
Chen & Tsong, PRL' 90, Nature' 91

Kellogg & Feibelman, PRL'90

DAS Model Si(111)-7x7



O_2/Si(111)-7x7: 300 C, 2V, 100 pA



Adatom sites:

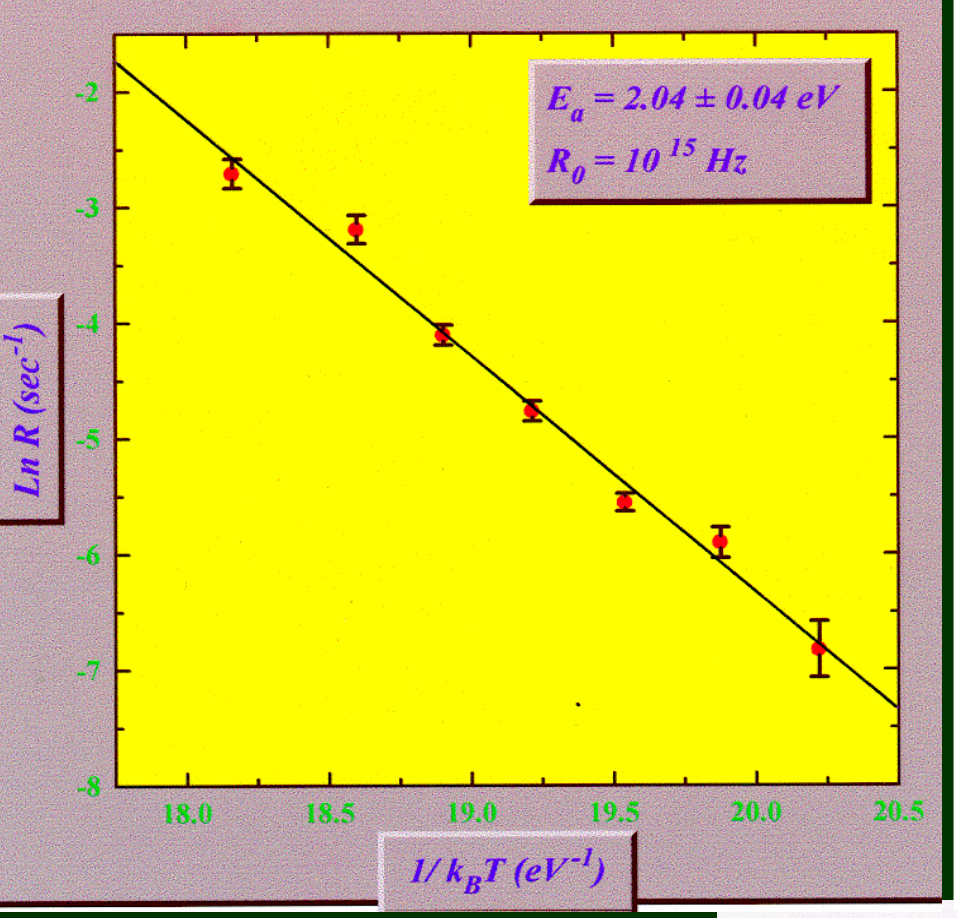
FE, FC, UE & UC

Rest-atom sites:

FR & UR

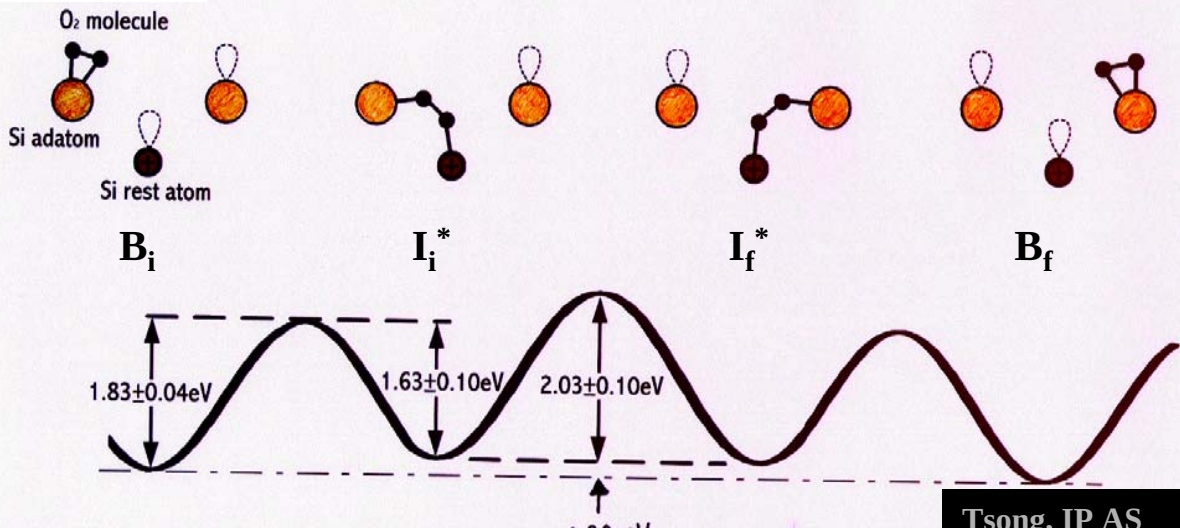
Takayanagi et al.

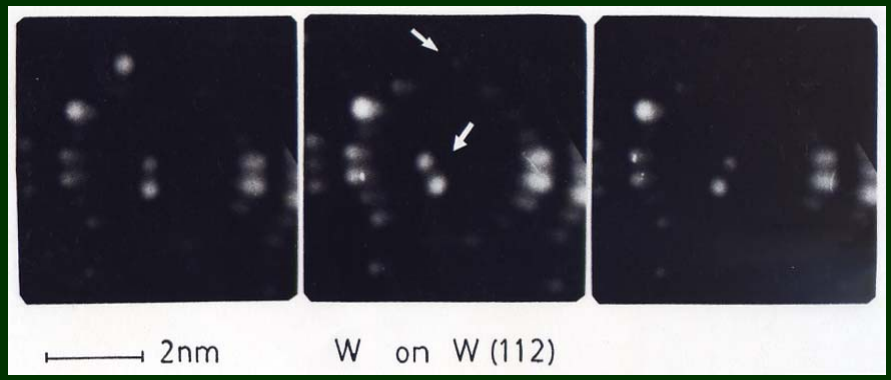
Hwang et al. PRL ’97
Tsai et al. PRB ‘02



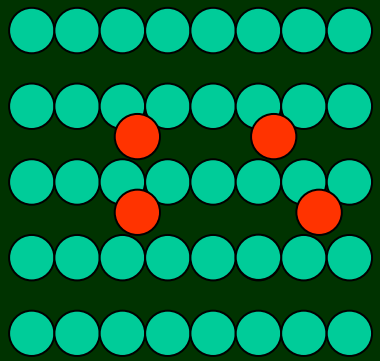
Site to Site	E_d	Log{ν_0(Hz)}
FE to FE	2.04 ± 0.04	15.0 ± 0.3
FE to FC	2.29 ± 0.06	16.2 ± 0.5
FC to FE	2.13 ± 0.11	15.6 ± 1.0
UE to UE	2.16 ± 0.04	15.9 ± 0.3
UE to UC	2.01 ± 0.10	14.6 ± 0.8
UC to UE	1.96 ± 0.13	14.1 ± 1.1
Intermediate State Hopping		
B_i to I_i^*	1.83 ± 0.04	13.0 ± 0.4
I_i^* to B_i	1.63 ± 0.10	13.2 ± 0.9
I_i^* to I_f^*	2.03 ± 0.10	16.1 ± 0.9

1. Site and path specific diffusion parameters
2. Diffusion mechanisms: Tumbling mechanism
3. Self-catalyzed oxidation



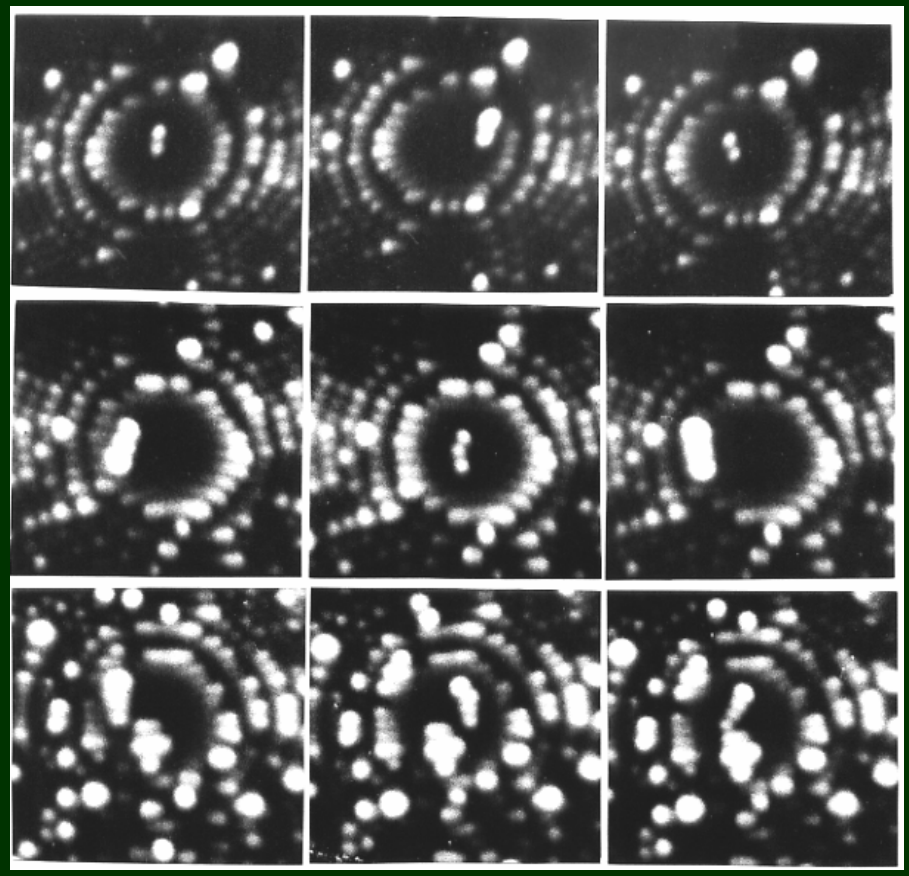


Tsong ‘72



1D diffusion:

Coupled motion of atoms in neighbor surface channels of W(112)

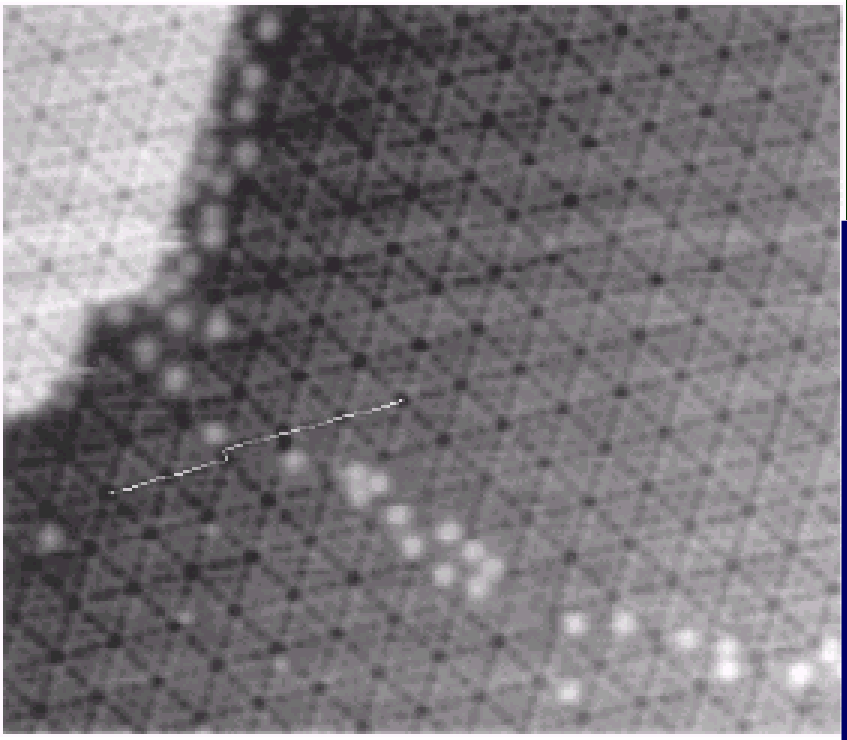


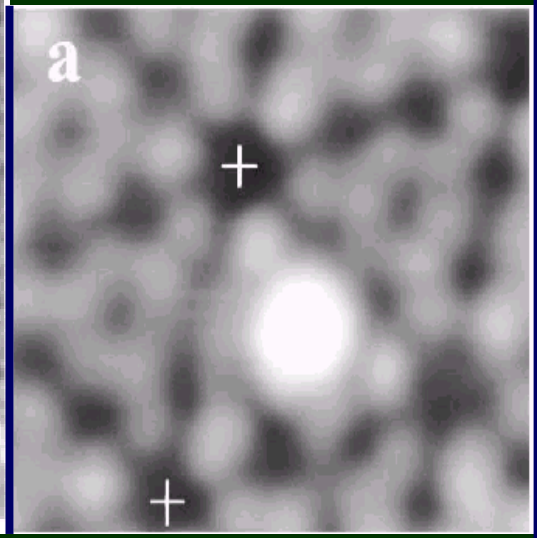
Bottom-up approach: controlled growth of atom-clusters and observing their diffusion-interaction, Hopping Diffusion

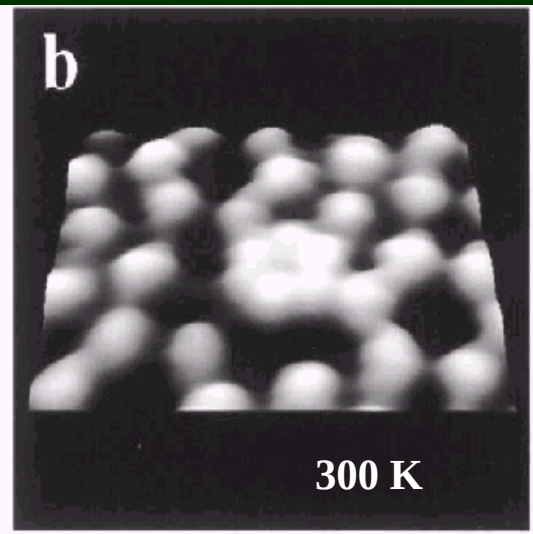
Si Magic Nanoclusters

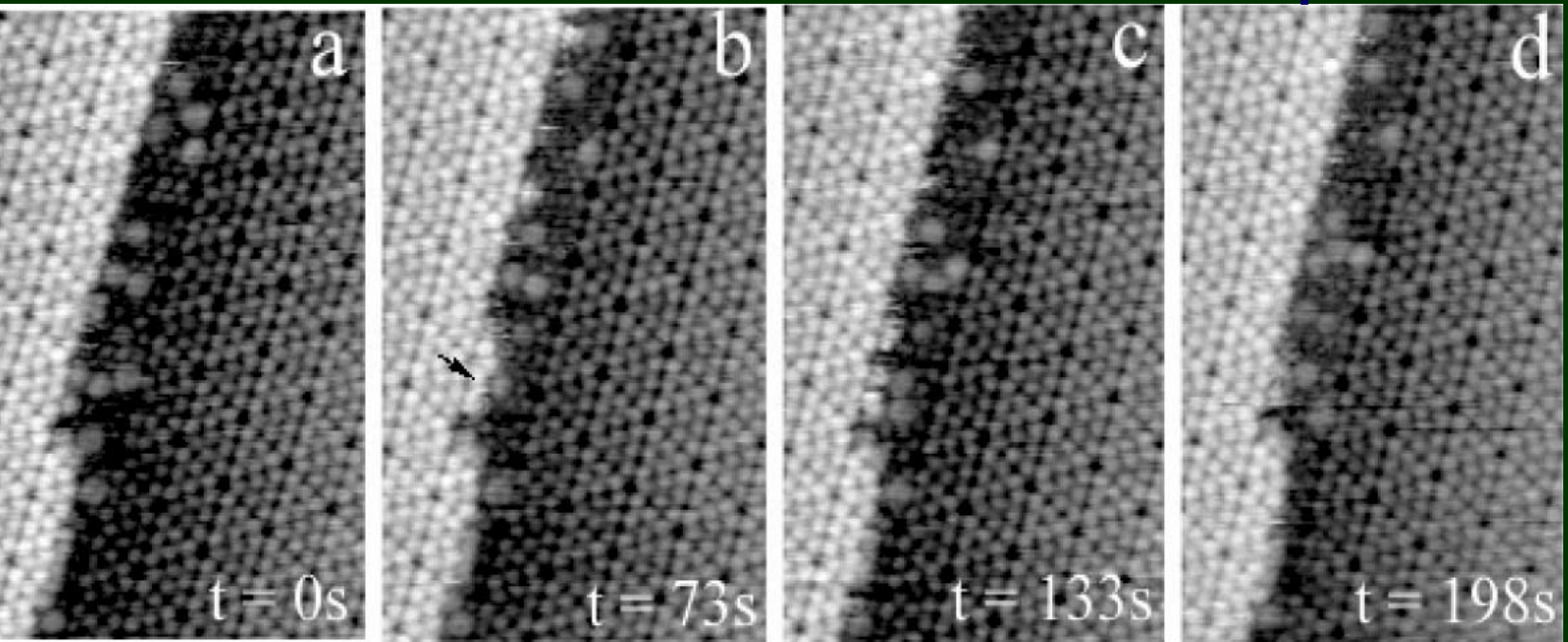
Surface Molecule-Like (~12 atoms)

The Basic Unit for Mass transport









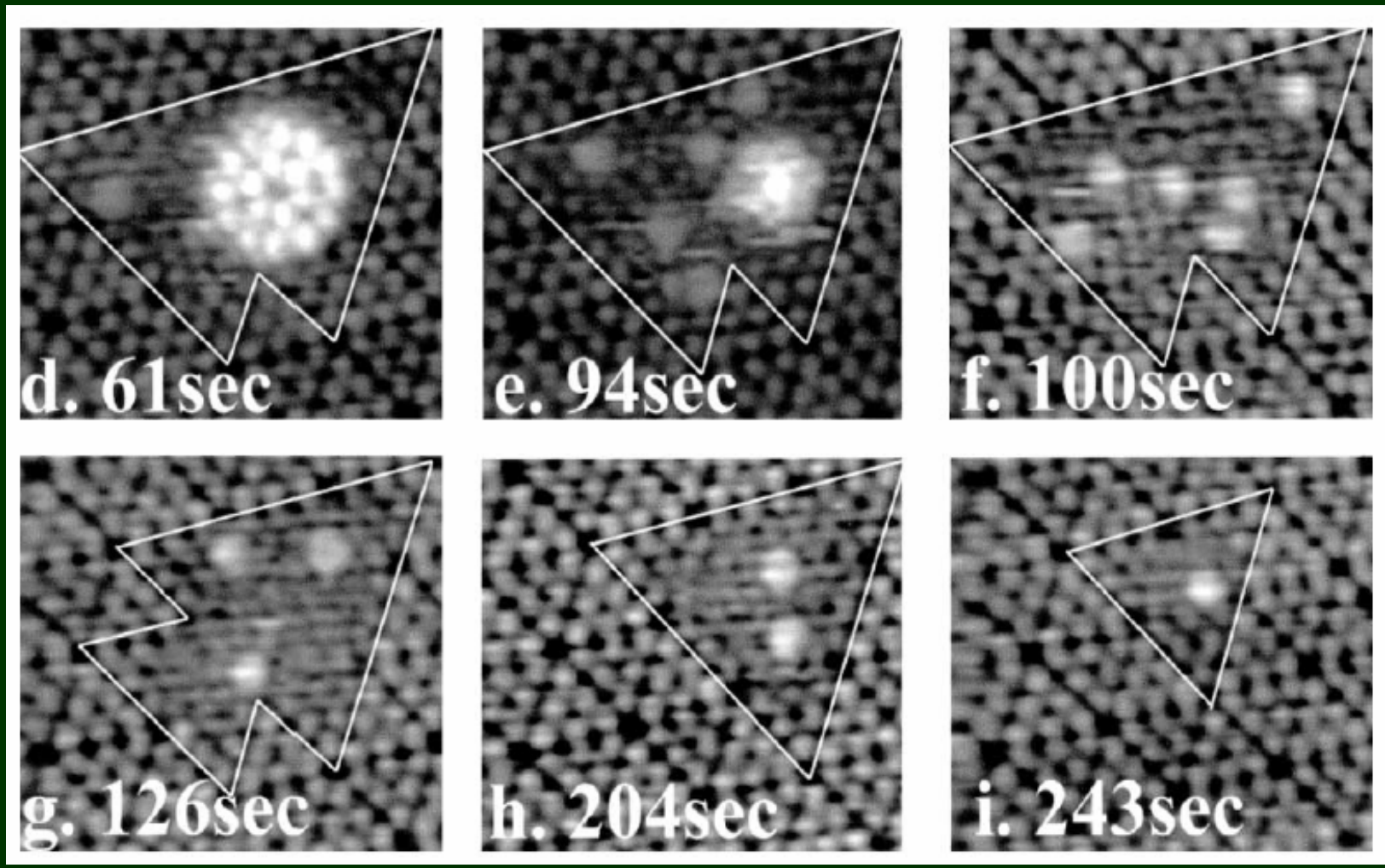
450 ˚C

Hwang, Ho & Tsong
PRL 83, 120 (1999);
Ho, Hwang & Tsong
PRL 84, 5792 (2000)

Dynamic detachment & attachment of Si magic clusters at step edges

Dynamics of Si Magic Clusters (Surface Molecule-Like) on Si(111)-7x7 at 450 ˚C

Atomic jumps occur in ps, microscopy images are time lapse-images



Electronic Effects on Adsorbate Interactions

On Metal Surfaces

Theoretical:

T. L. Einstein & J. R. Schrieffer (73); K. H. Lau & W. Kohn (78)

K. A. Fichthorn & M. Scheffler (00), and many more

Experimental:

FIM: Mostly on W(110) surface

Tsong (72, 73), Casanova & Tsong: (80, 81): Pre-PC image digitizer

Watanabe & Ehrlich: (89, 91, 92): PC image digitizer available

STM: Cu(111) surface, quasi 2D system

J. Repp et al. (00) (Rieder) N. Knorr et al. (02) (Brune)

Silly et al. (03) (Schneider)

Basic Features: pair interaction vs. potential of mean force

1. Weak 2. Long range 3. Oscillatory

Review: T. T. Tsong, Rep. Prog. Phys. 51 (99) 759 Before STM Studies

M. L. Merrick, W-W. Luo and K. A. Fichthorn, Prog. Surf. Sci. 72 (03) 117.

Adatom-Adatom Interaction in 1-D: Pd-Pd on W(112)

(a) In same channel

(b) In 1st nn channels

(c) In 2nd nn channels

(d) In 3rd nn channels

X: lateral separation

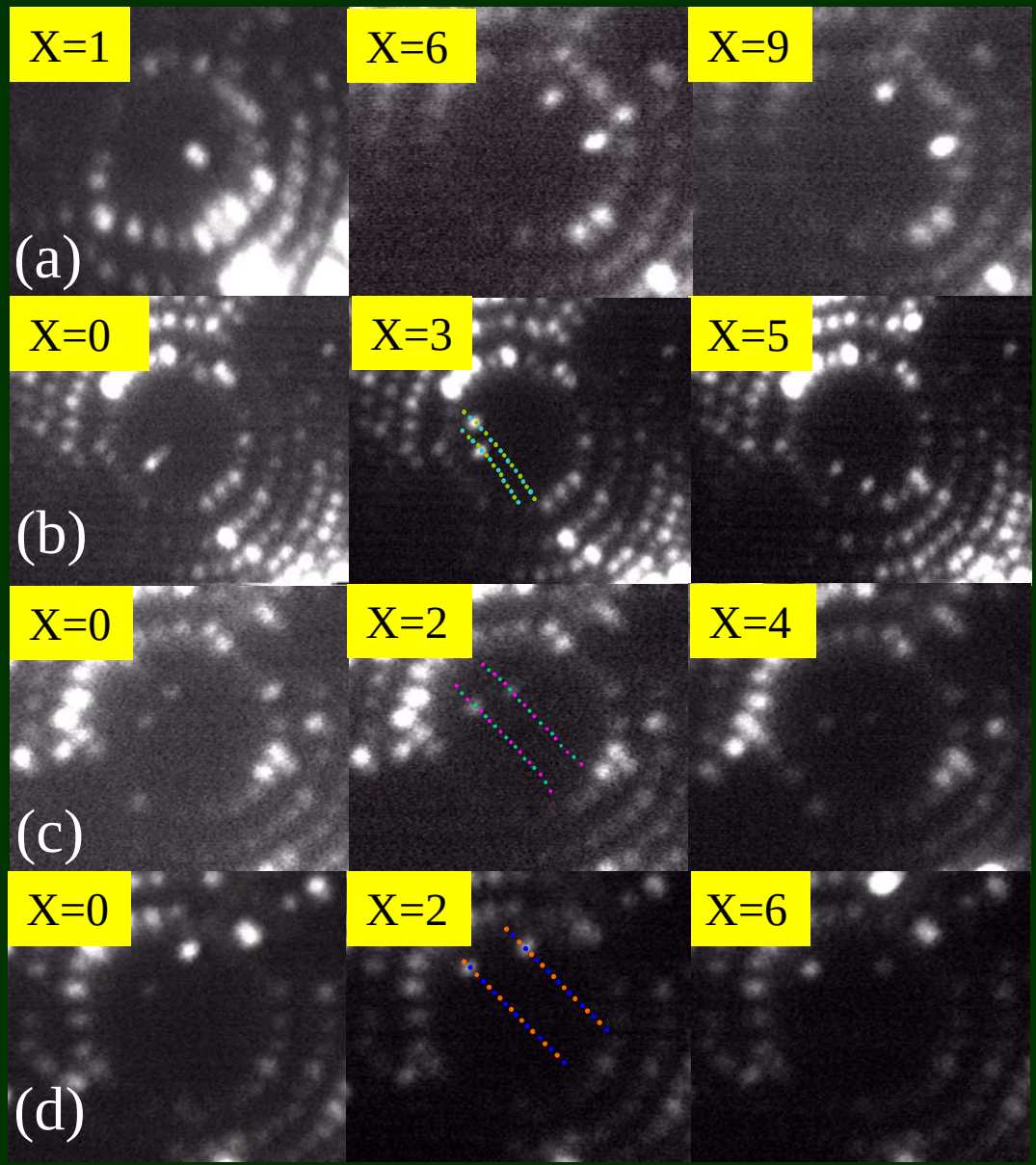
In the same channel:

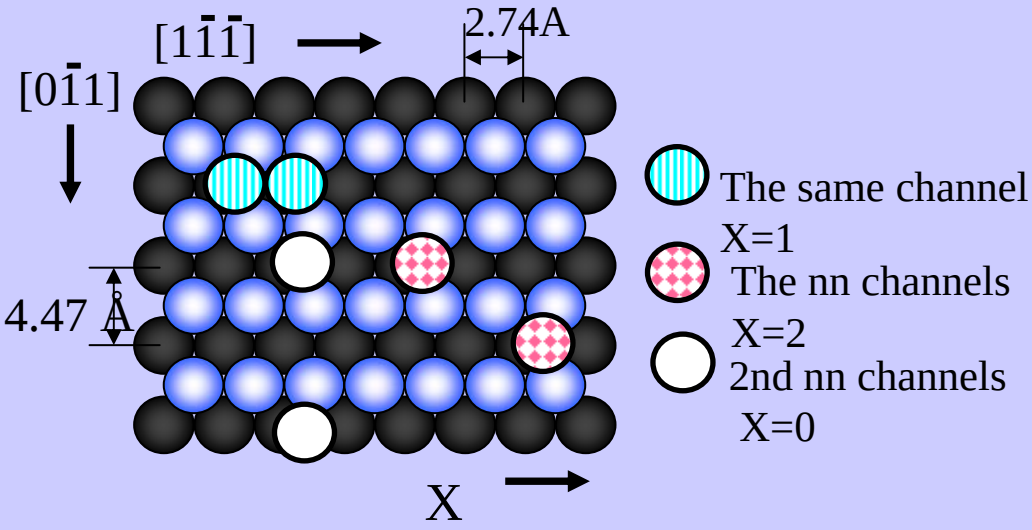
$E_d(Pd) = 0.32 \pm 0.02$ eV

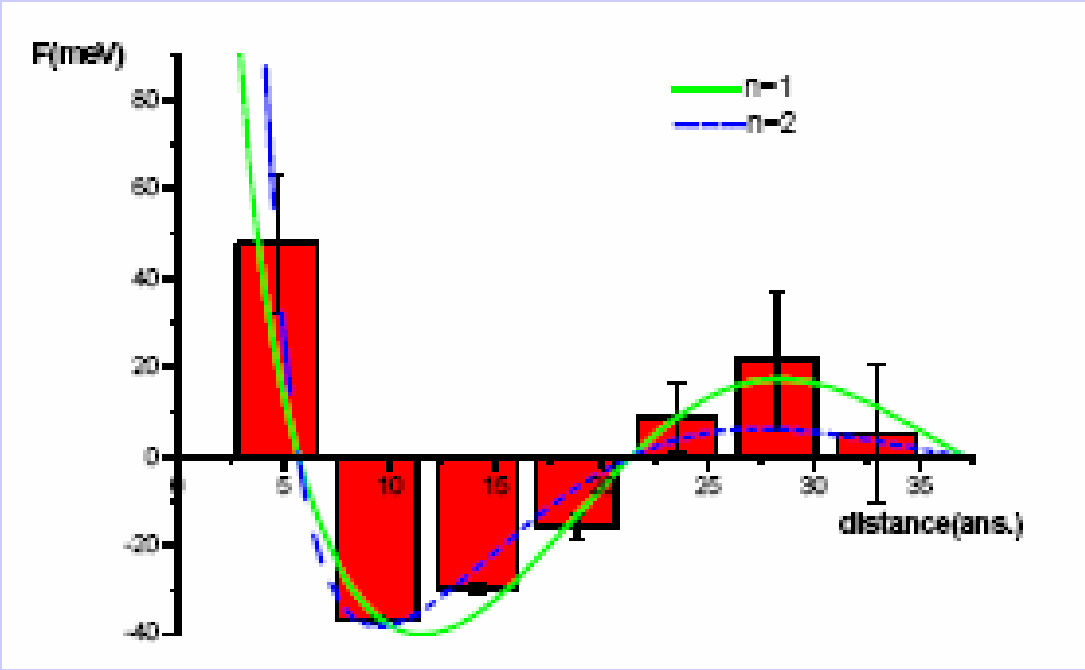
$E_d(Pd_2) = 0.59 \pm 0.05$ eV

$E_b(Pd) = 0.61 \pm 0.03$ eV

Fu et al. '03







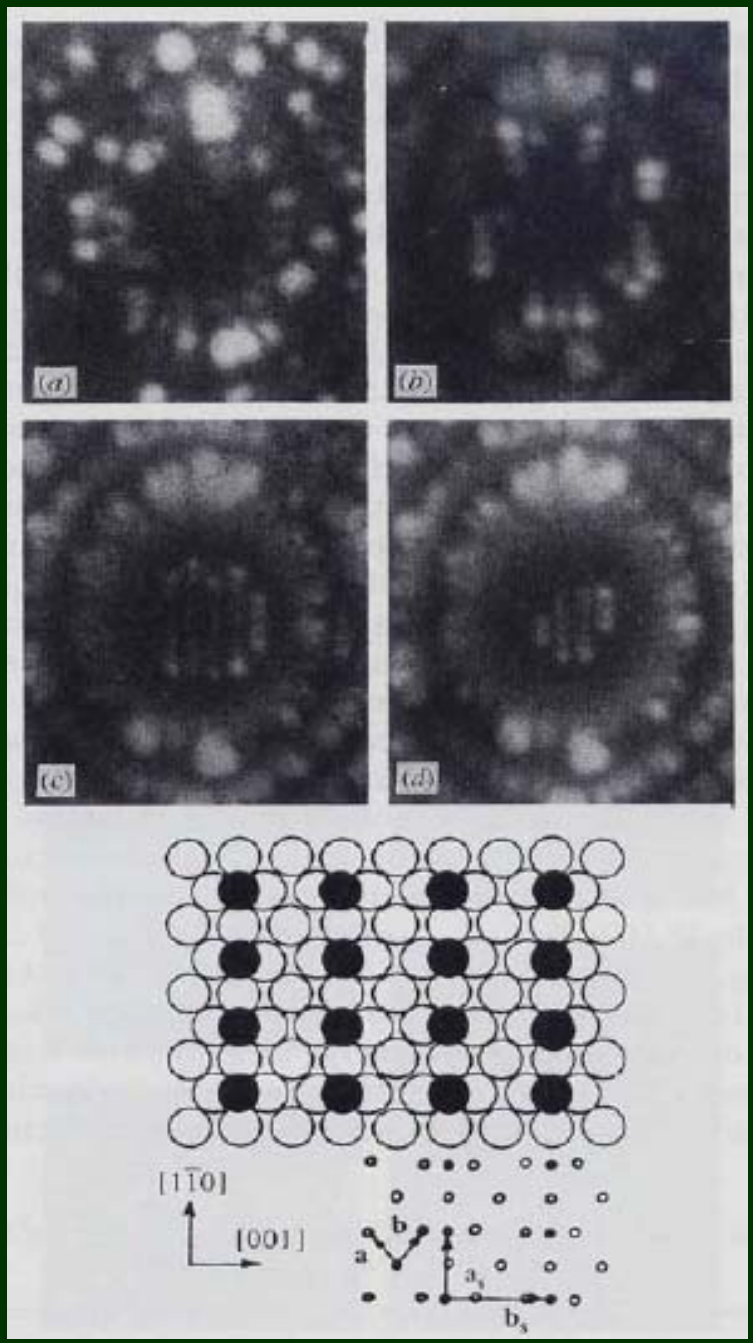
Pd-Pd nn-channel interaction, data taken at 248 K

Best fit curve:

$\cos(2k_FR)/(2k_FR)^n$ for n=1

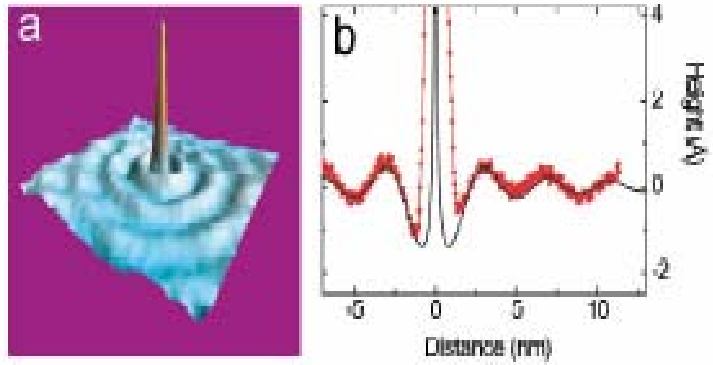
$k_F = 0.3$ Å^{-1}

Tsong & Casanova, PRL ‘82

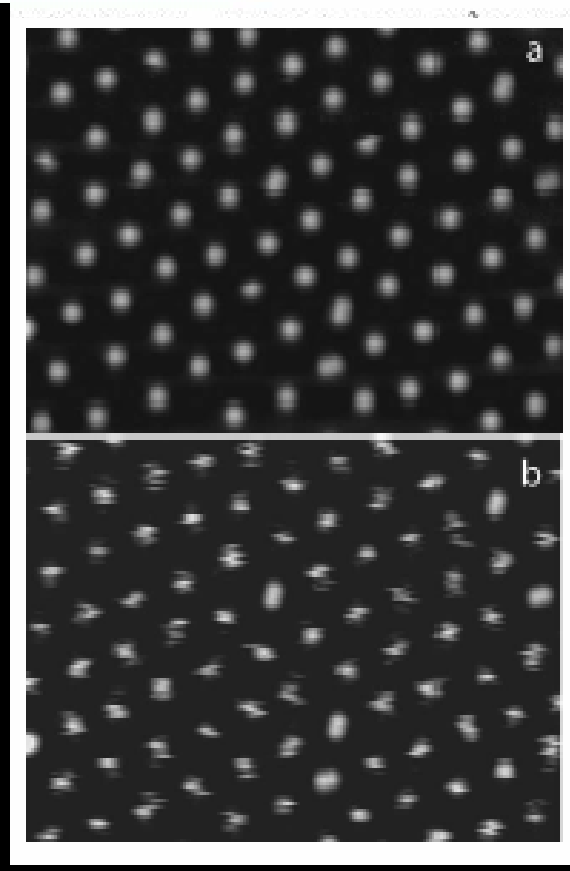


Si on W(110)

Silly & Schneider et al. PRL ‘04



Correlation between Adatom-adatom interactions & Adlayer structure

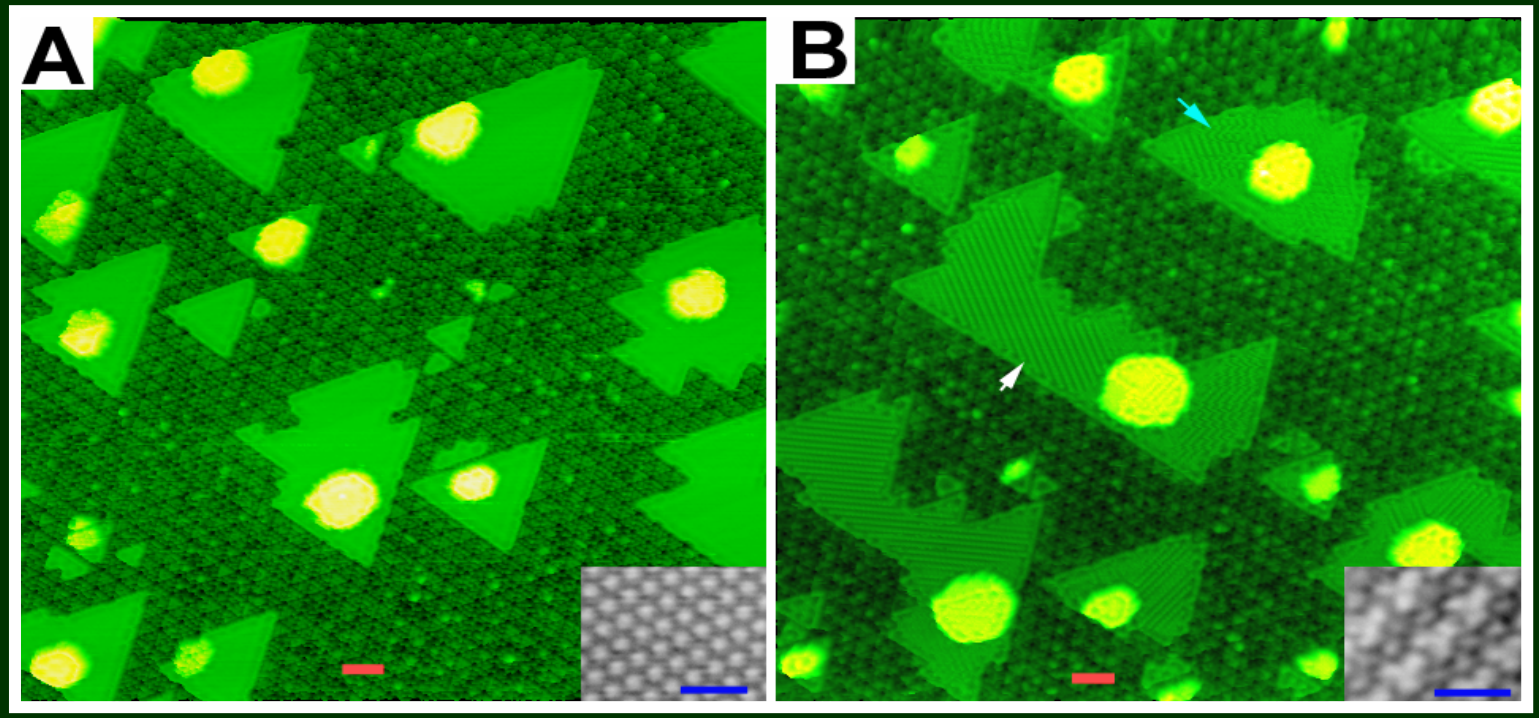


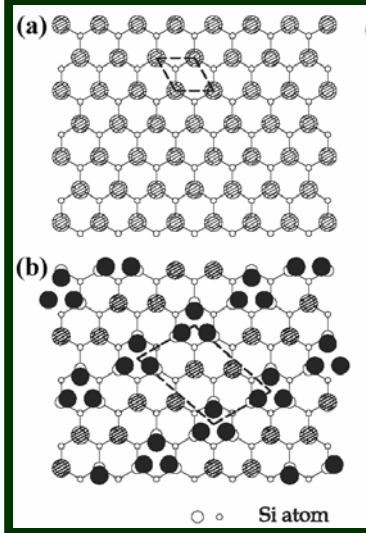
Ce on Ag(111)

A Mesoscopic Quantum System: Pb Nanoislands on Si(111)

Size Dependence of a Low T Phase Transition of 2D Nano-Islands

Pb(1x1) (a brief heating to 400 ºC) ↔ Pb(√7x√3) on Si(111)-7x7

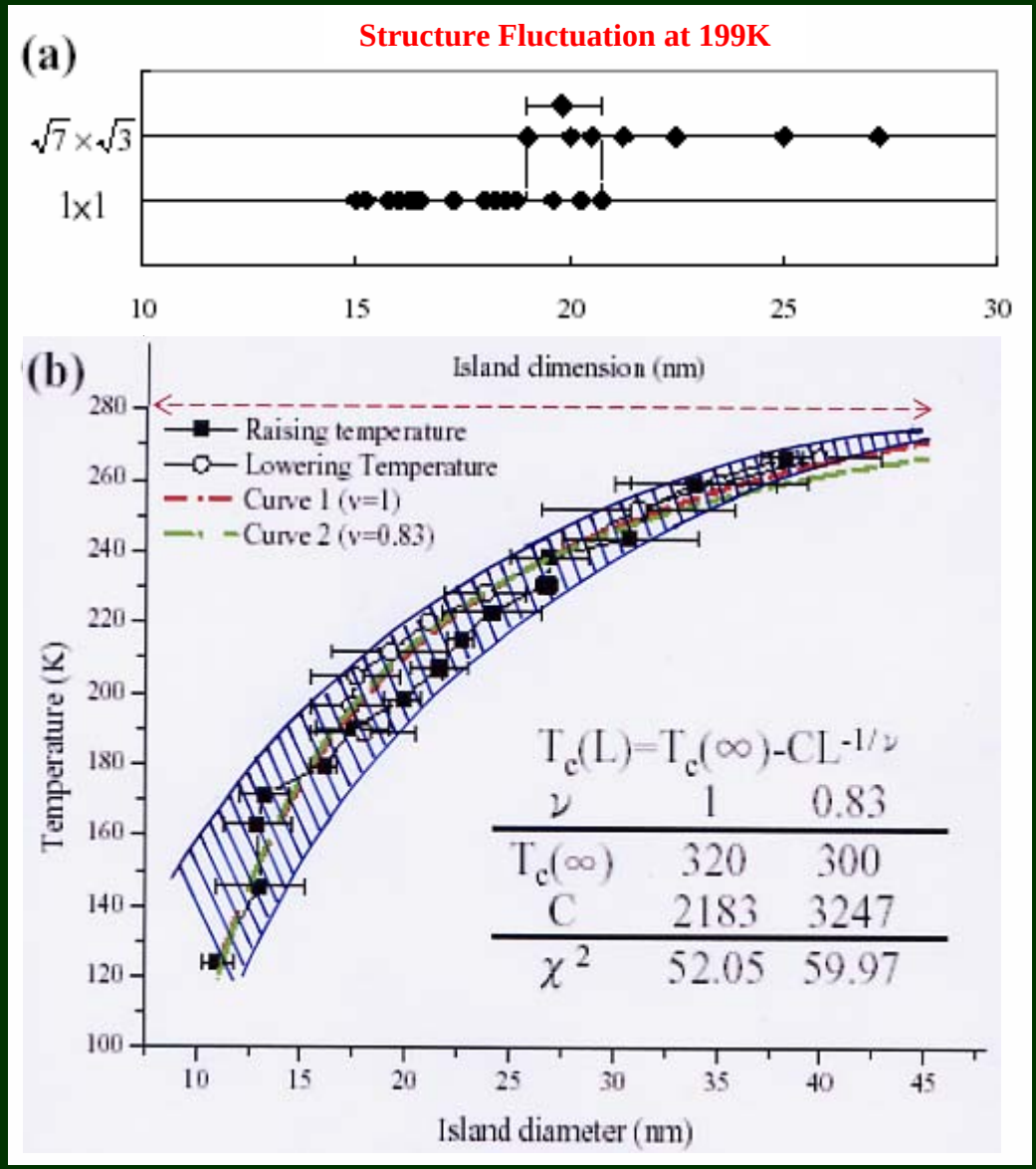




300 K, red bar = 5 nm, blue bar = 1 nm

190 K, T_t is lower for smaller domains

Landau-Lifshitz: continuous phase transition if low T phase is a subgroup of high T phase, thus temporal & spatial fluctuations can be obseerved.



Hwang et al. (PRL '04)

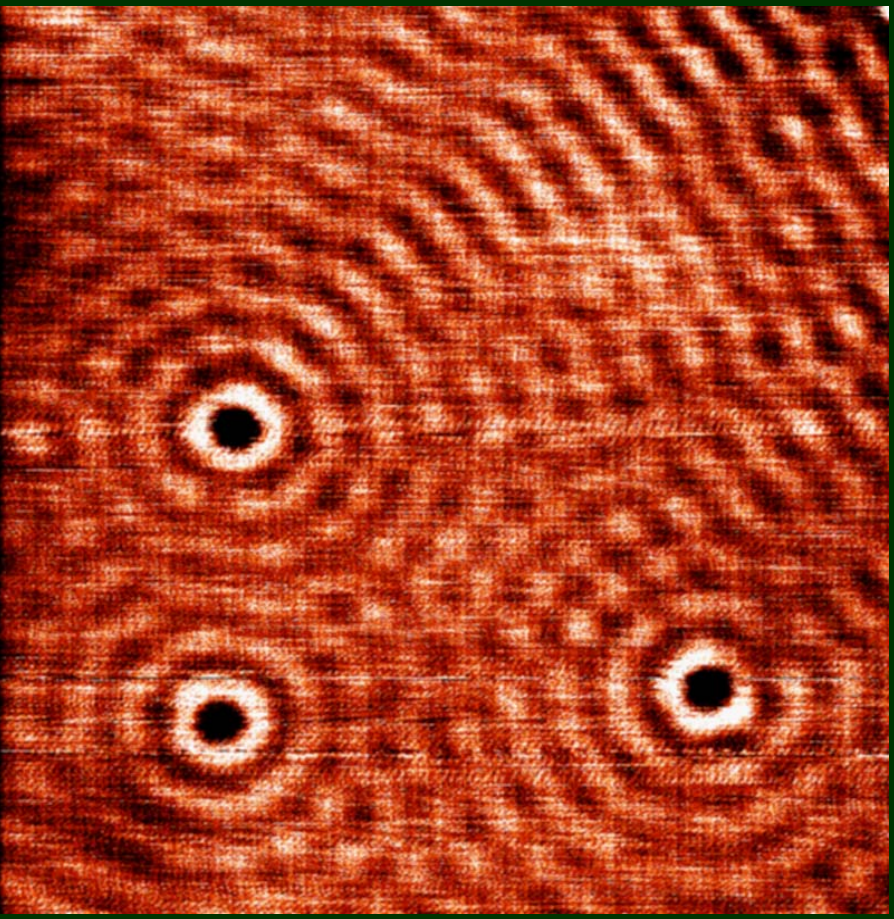
Finite Size Effect of T_t

There is no well defined transition temperature for finite size nano islands in a structure "phase transition" !

Finite 2D nano islands on infinite substrate: Weak coupling between islands and substrate

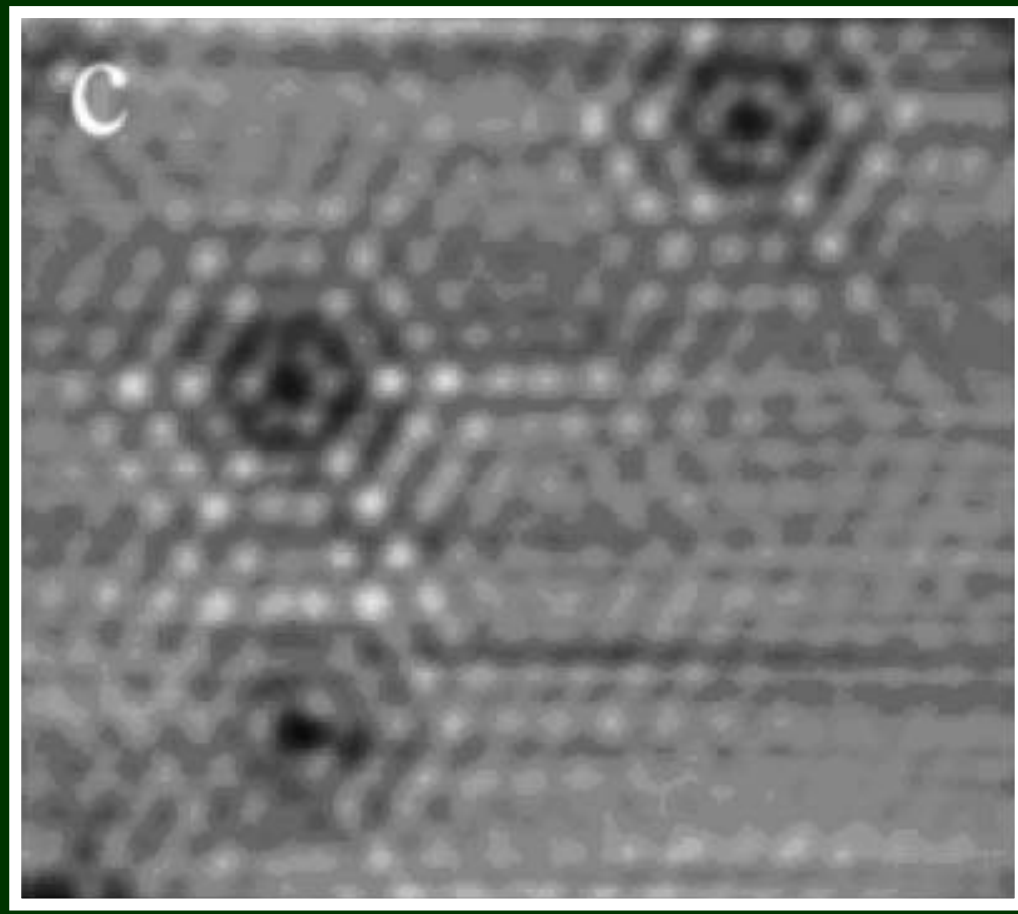
Analysis based on Ising Model (ν=1) & 3-State Potts Model (ν = 0.83).

Electron Wave Interference Pattern by Impurity Atoms



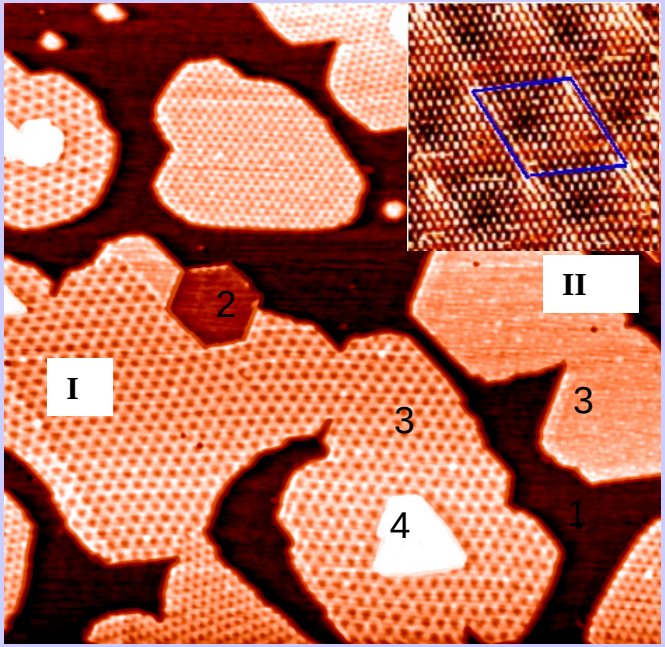
Eigler et al. Nature ’91
Su et. al.: Cu(111)

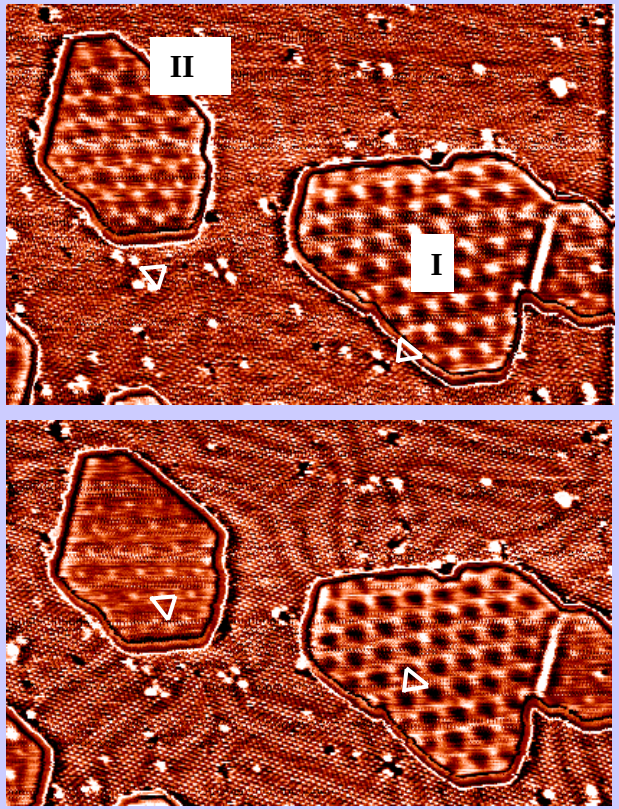
Atomic Structure Modulation Around Adsorbed H-Atoms



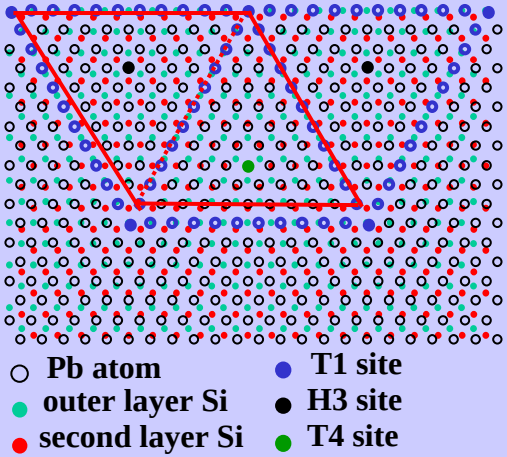
H/Pb/Si(111), Hwang & Chang et al. PRL ‘04

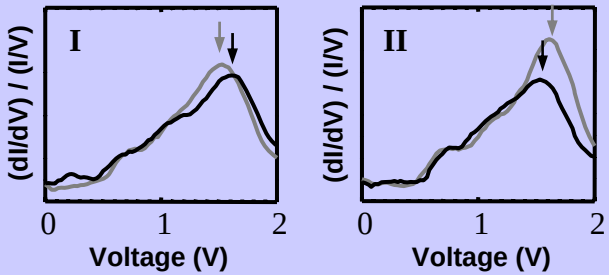
Electronic Morié Pattern of Pb-Si Interfaces (IC Phase) of Type I & Type II Quantum Islands



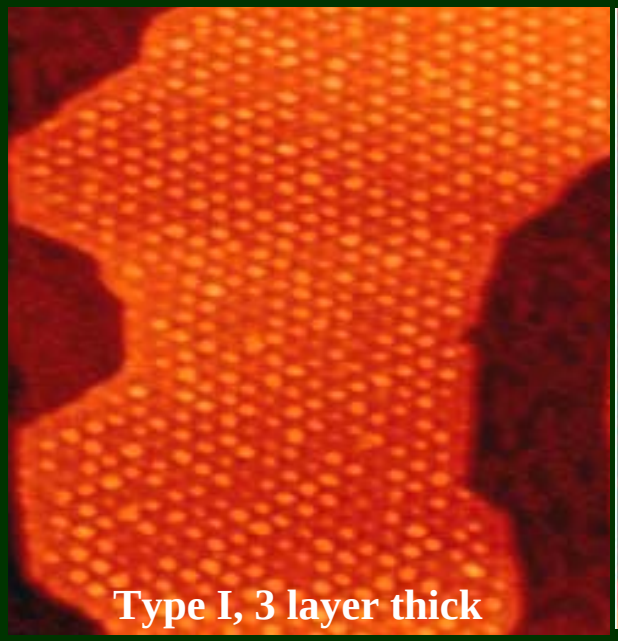


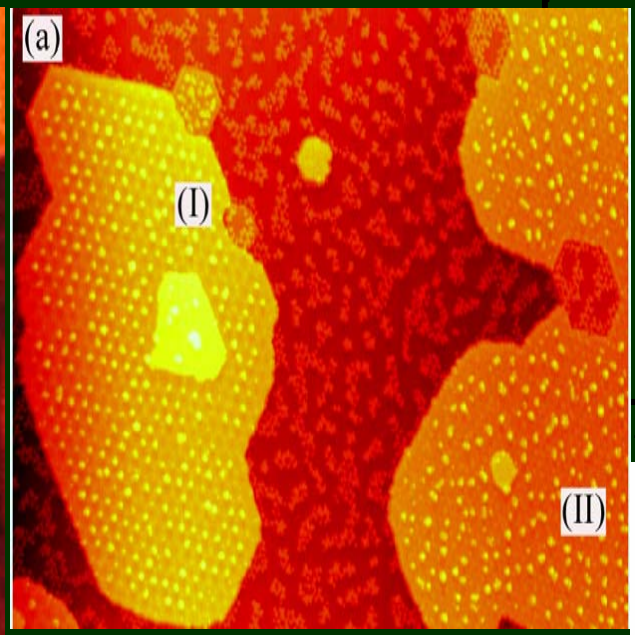
W-B Jian et al., PRL 03

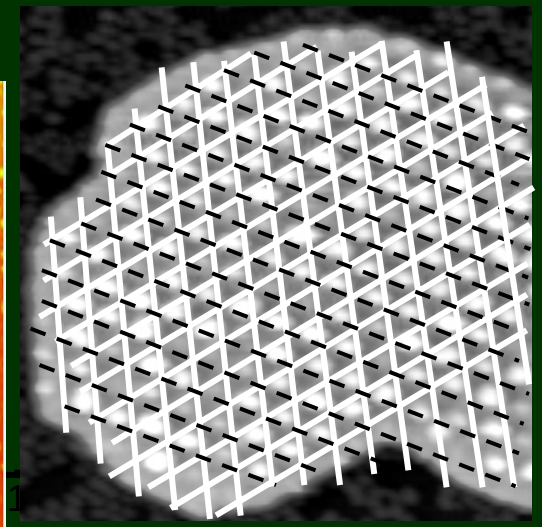


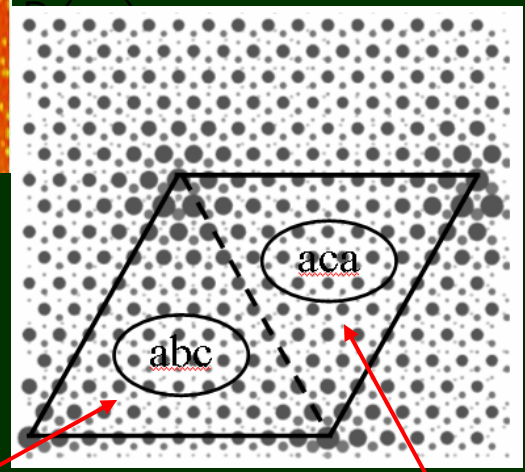


Electronic Moriè Pattern as Template:
Ag nanopucks (one-layer thick) on quantum Pb islands of 3-layer thick





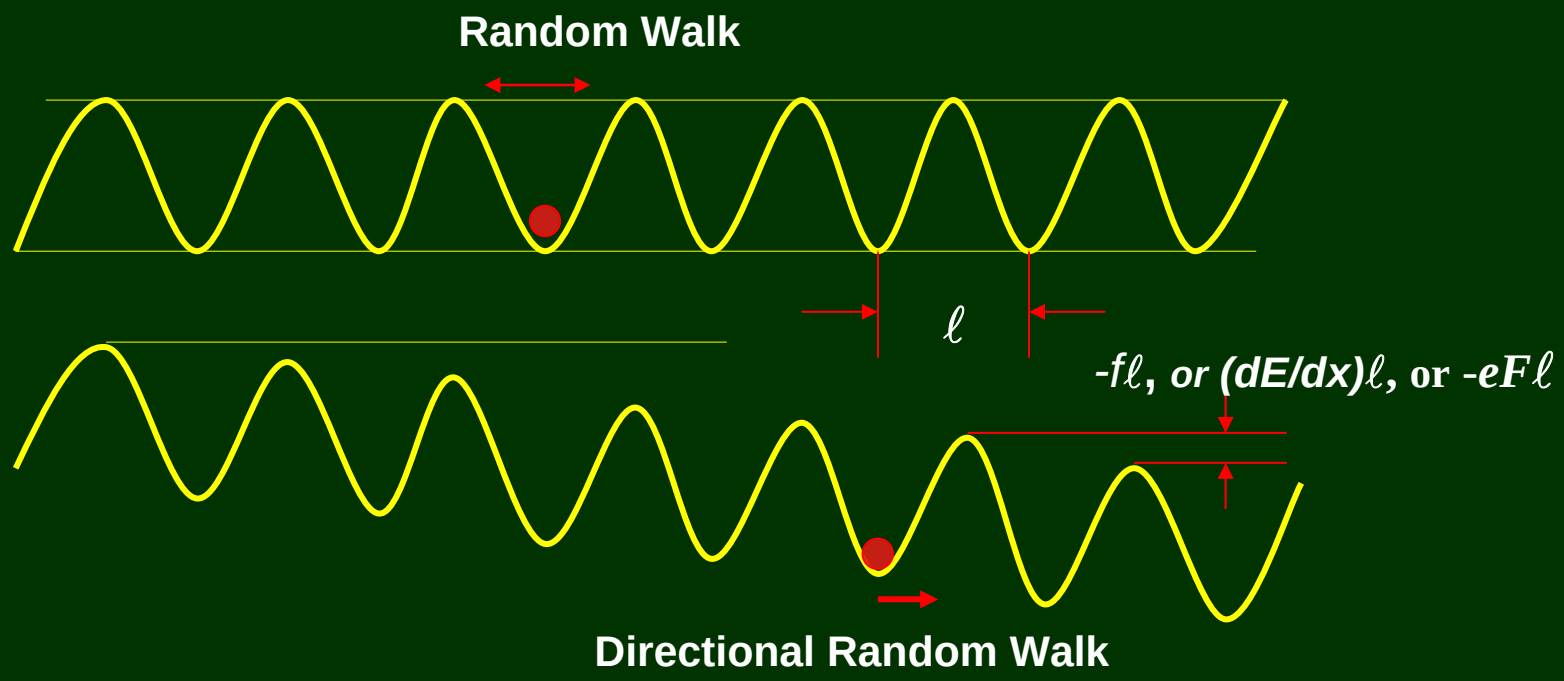




90 nm × 90 nm
ϑ= 0.25 ML
T = 120 K

100 nm × 100 nm
ϑ= 0.2 ML
T=120K

Chang et al.
PRL'04



Chemical Potential Gradient Induced Directional Walk:

Field gradient induced directional random walk

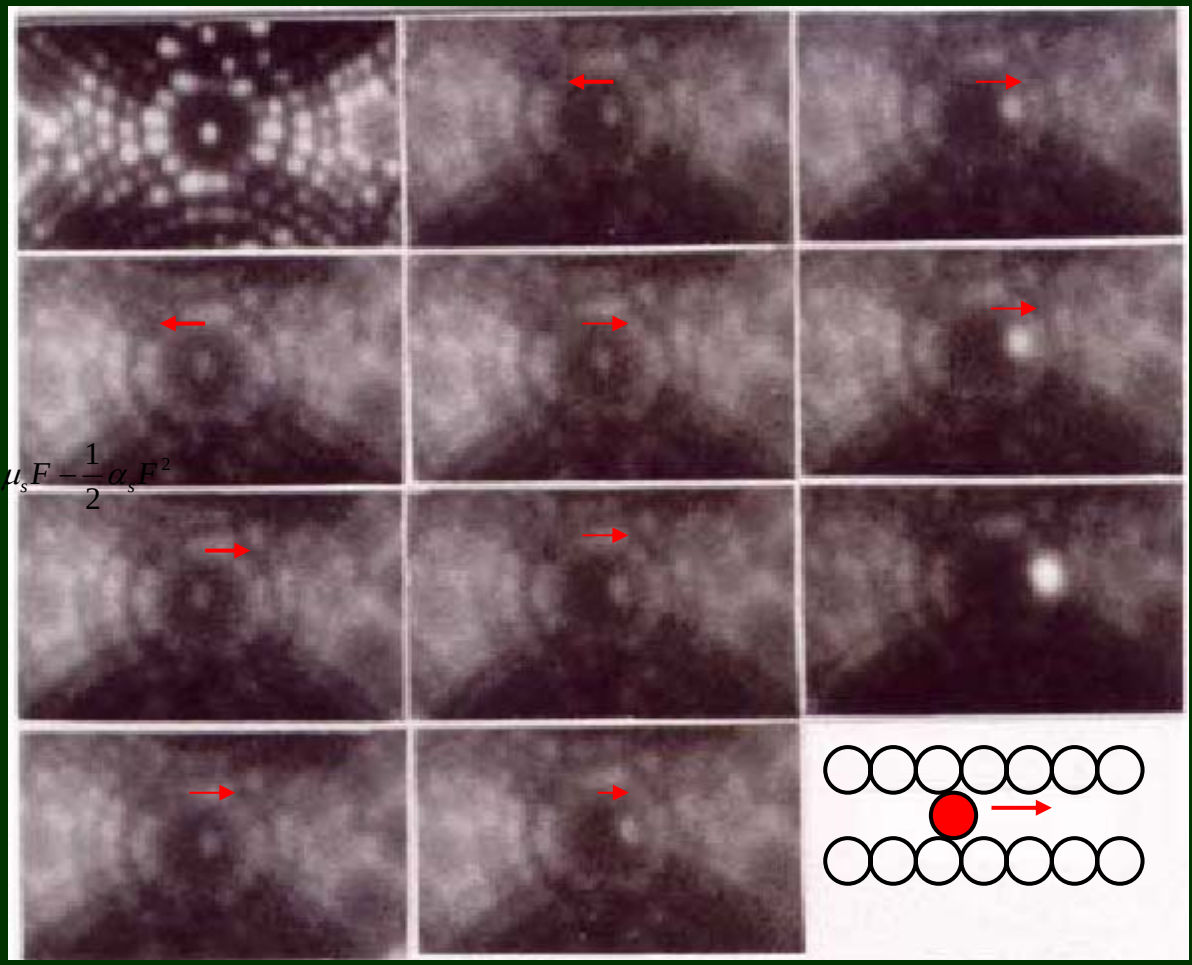
CP gradient can be produced by interactions, conc. & thermal grad.

Non-equilibrium thermodynamics: **kinetic effect!**

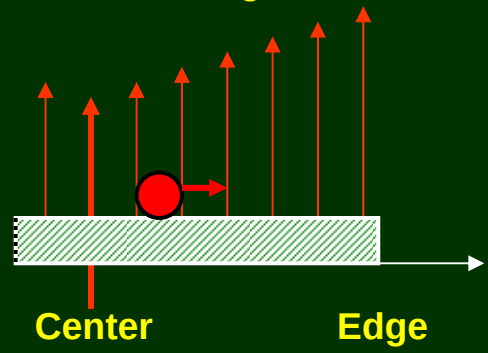
$E_p = -\mu_s F - \frac{1}{2}\alpha_s F^2$

Directional Walk of W on W(112)

Produced by Chemical Potential Gradient (Field Gradient)

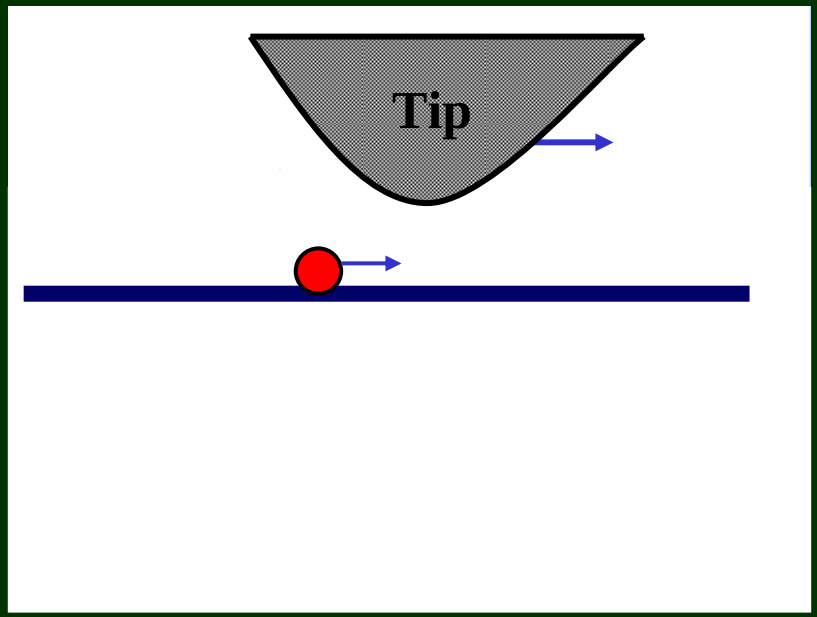


$F = F_C + \beta\rho$



$E_p = -\mu_s F - \frac{1}{2}\alpha_s F^2$

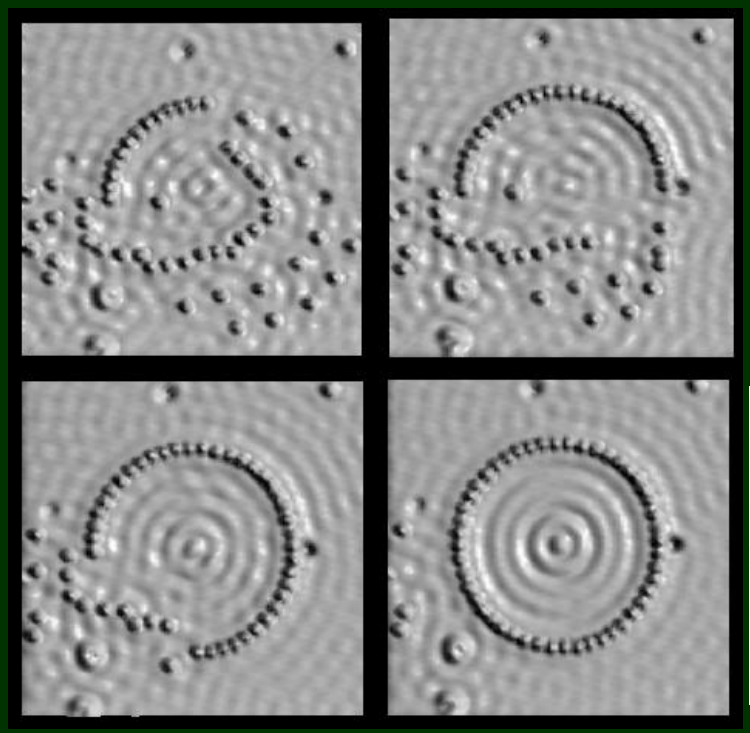
Tsong, Walko, Kellogg, Wang ‘72, ’75 ‘82



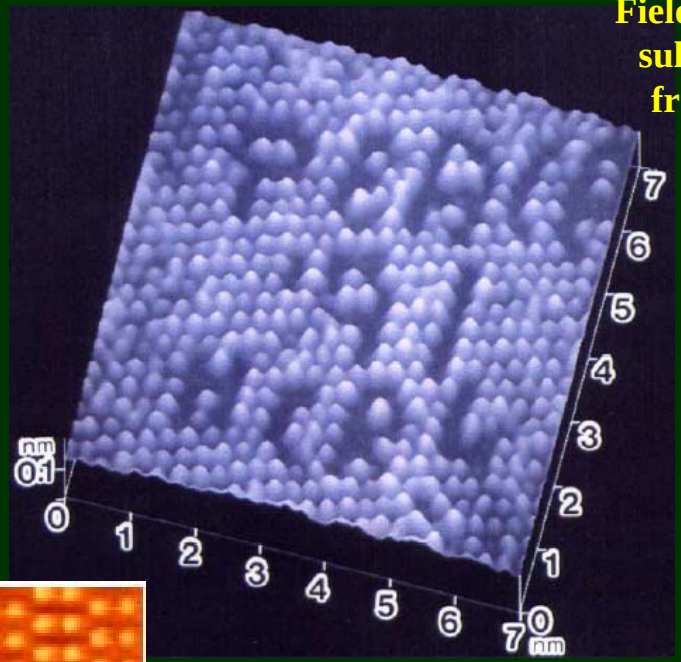
Atomic & Molecular Manipulation Using STM

Intrinsic interaction: Eigler et al. ’90

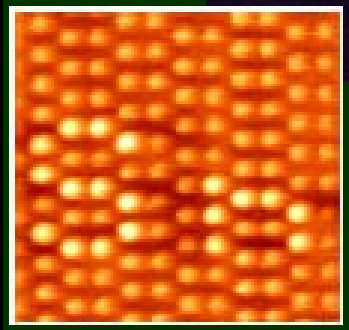
Field evaporation: Hosoki et al. ‘91



Fe/Cu(111)



Field evaporate sulfur atoms from MoS_2 surface

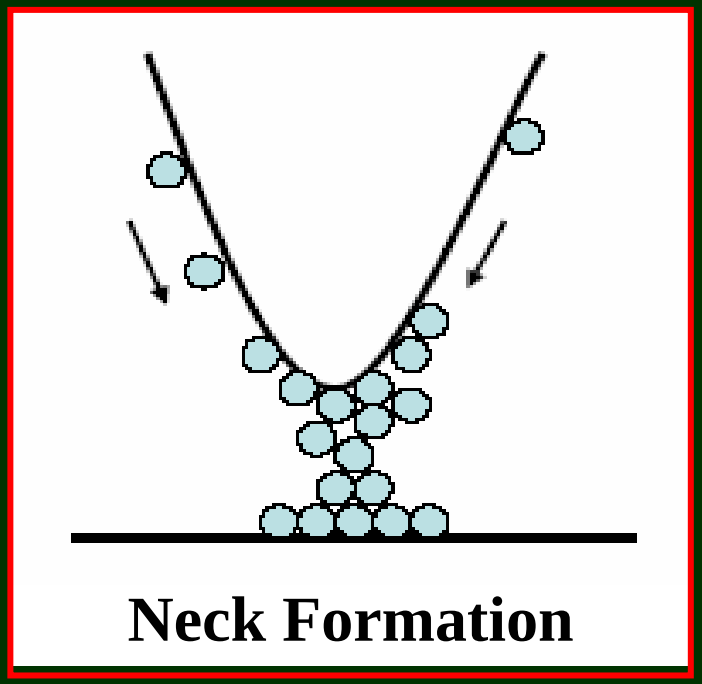


AFM manipulation of inlaid Sn atoms in Ge (111) Sugimoto & Morita et al. ‘05

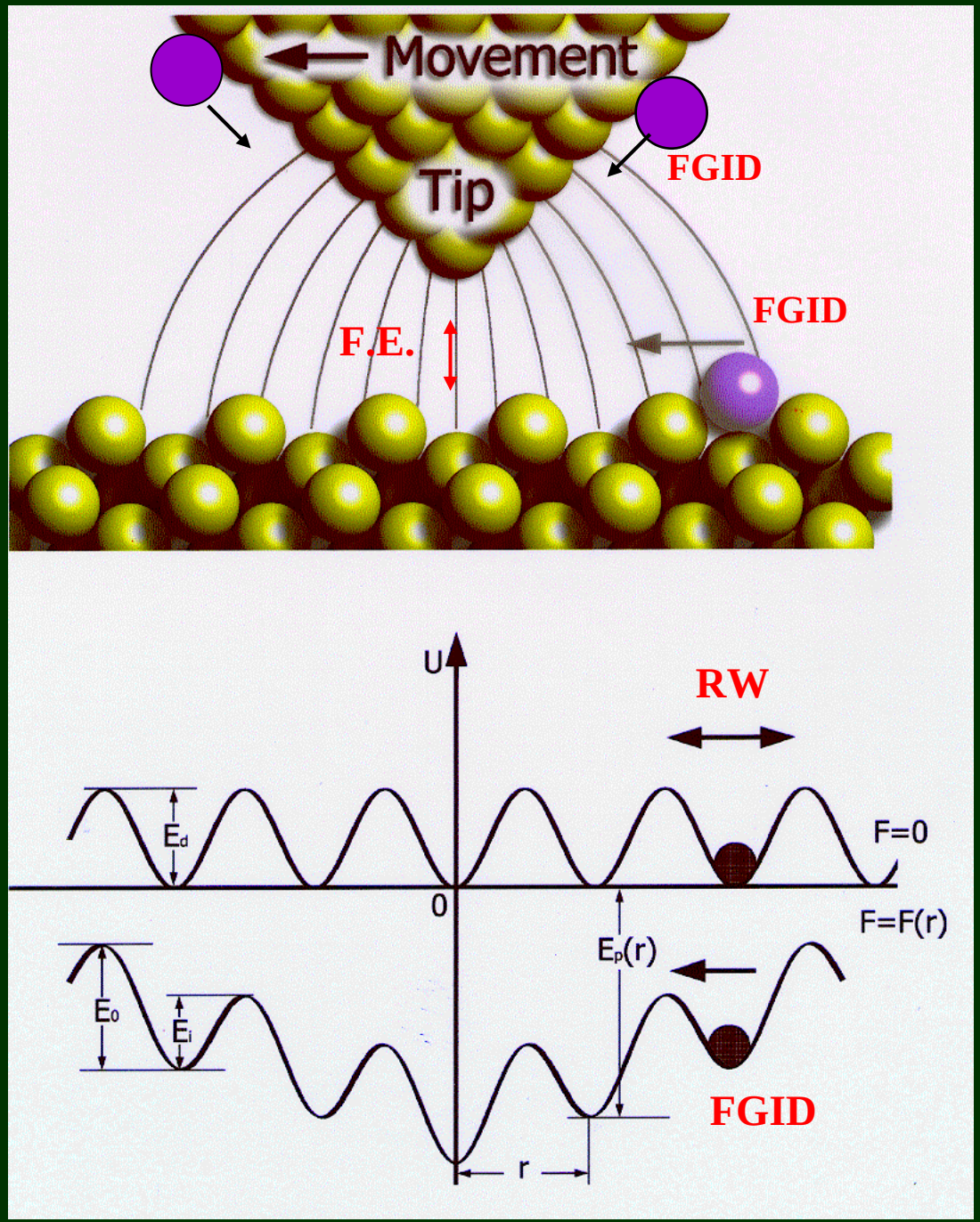
Some Other Methods of Atomic Manipulation

Tsong PRB '91

1. Field Gradient Induced Diffusion:
   Directional walk. Neck formation.
2. Field Evaporation:
   Atom transfer between tip & sample



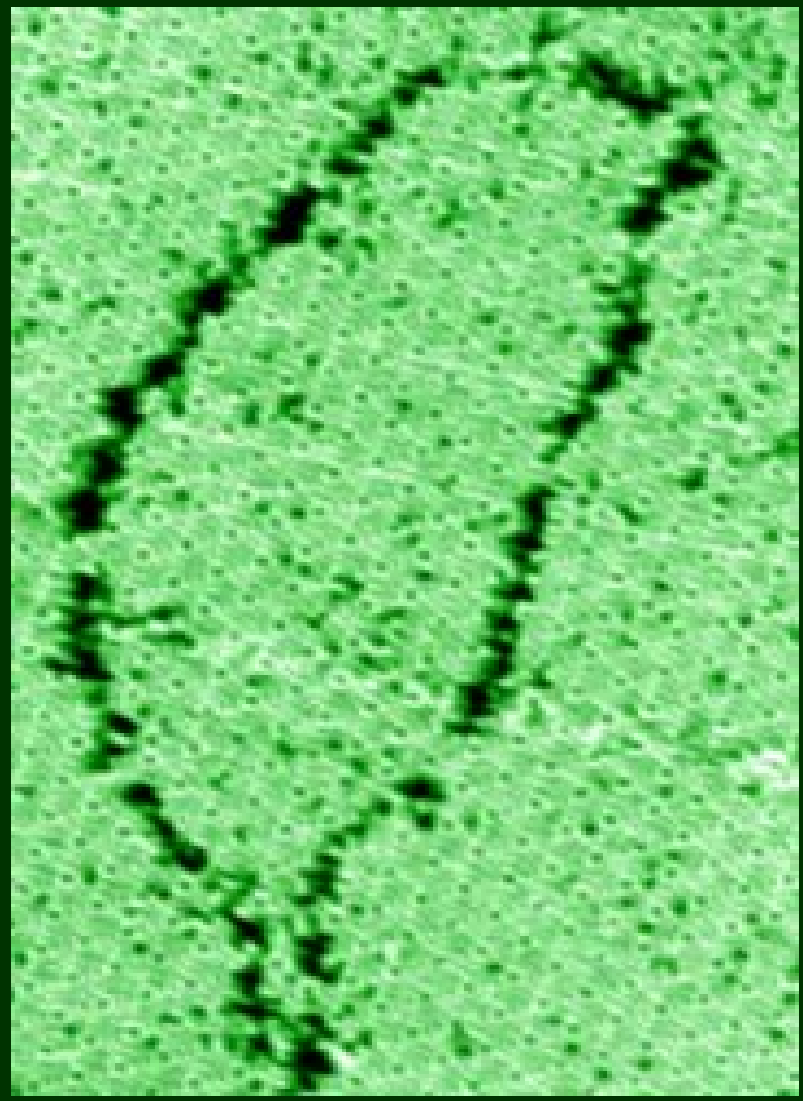
Neck Formation



Manipulation in nanoscale

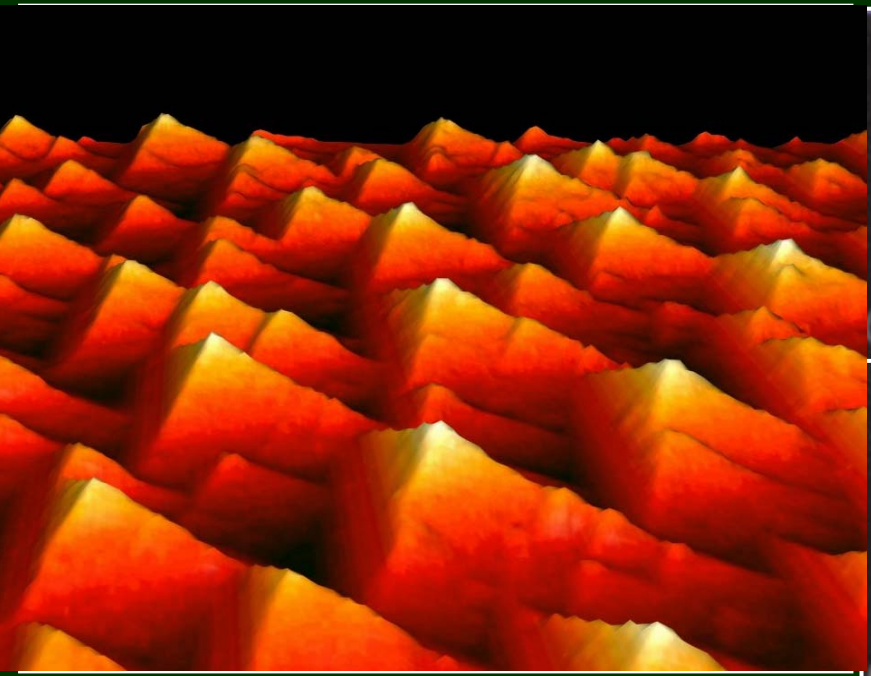
Thermally stable at 300 K

Neck Formation (700 x 1000 nm)



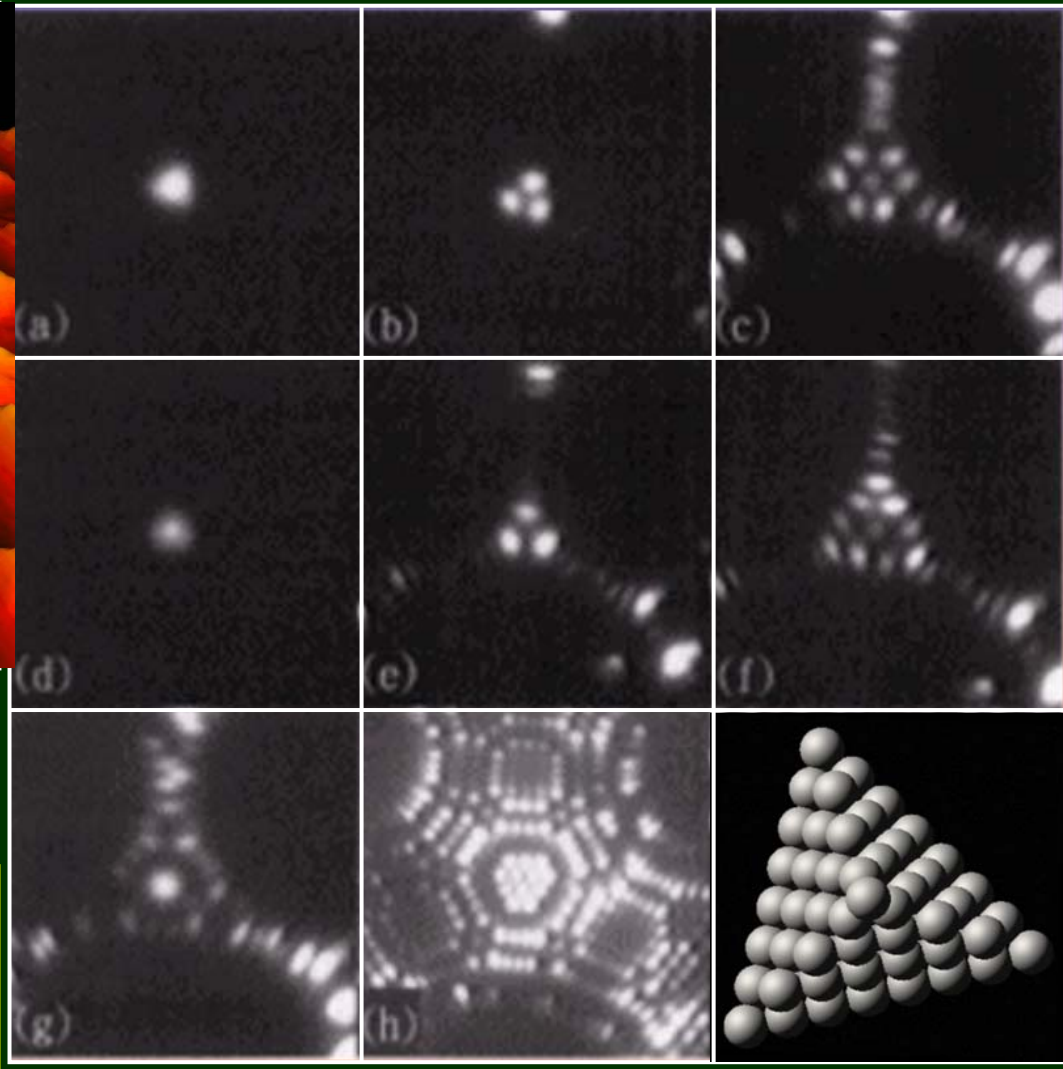
Field Evaporation (70 x 100 nm)

CPG (surface energy diff.) induced thermally & chemically stable & reformable Atom Perfect nm-size Pyramidal Tip



T. Madey et al.: Formation of pyramids by two comp. systems

Fu *et al.* PRB '01; Kuo et al. Nano Lett. '04



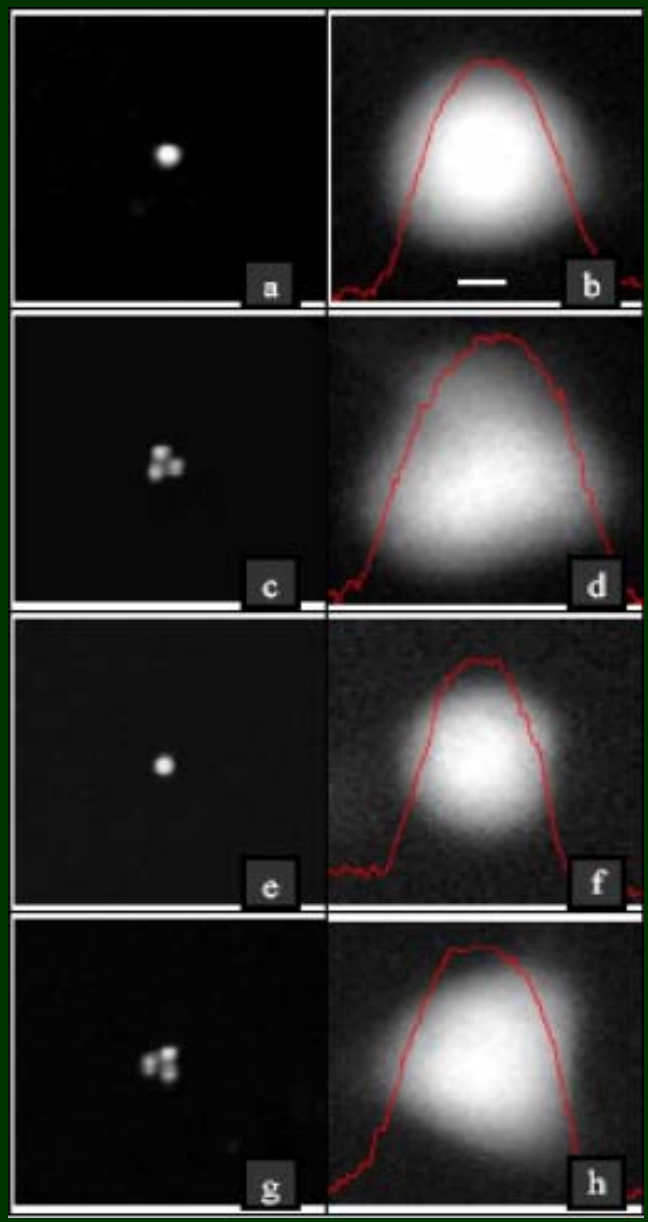
Atom perfect & chemically inert Pd-covered W(111)-base pyramid. Thermally stable up to ~1000 K, h ~ 1.4 nm

1 STM chemical mapping
2 Coherent electron beam for electron holography
3 Point ion source appls.

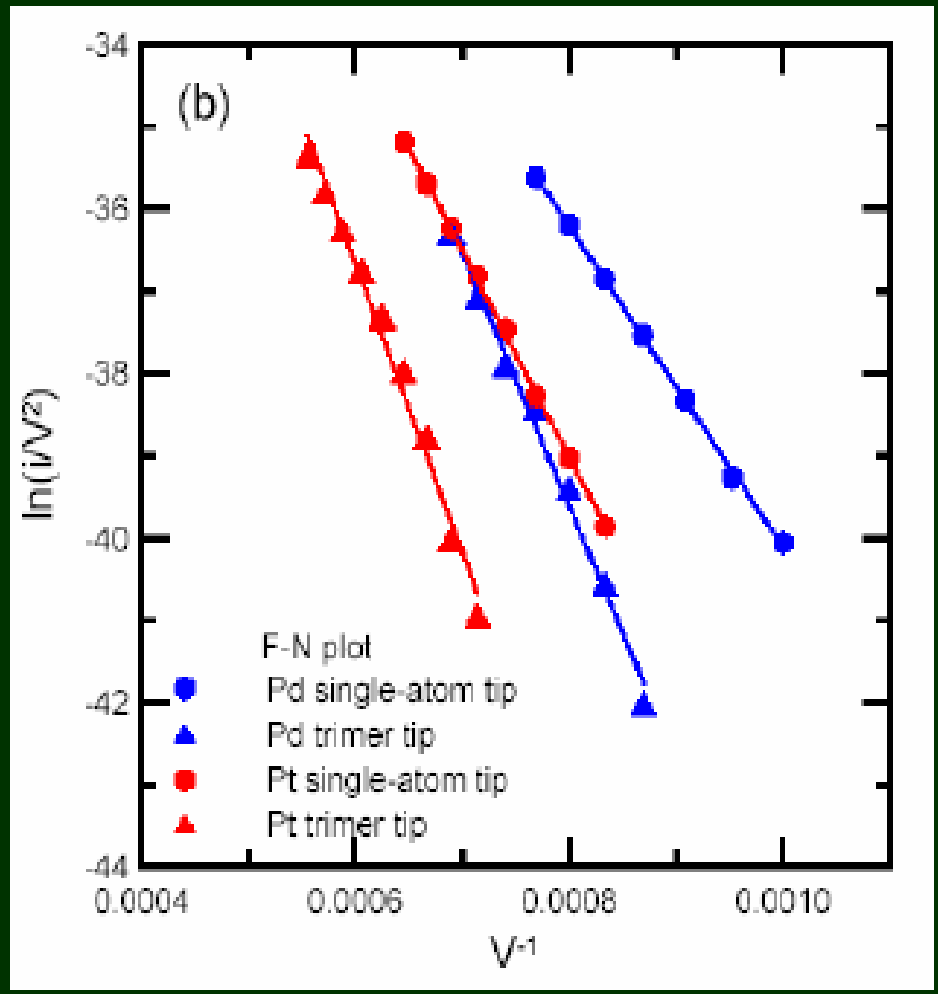
FI Source FE Source

Pd on W(111)

Pt on W(111)

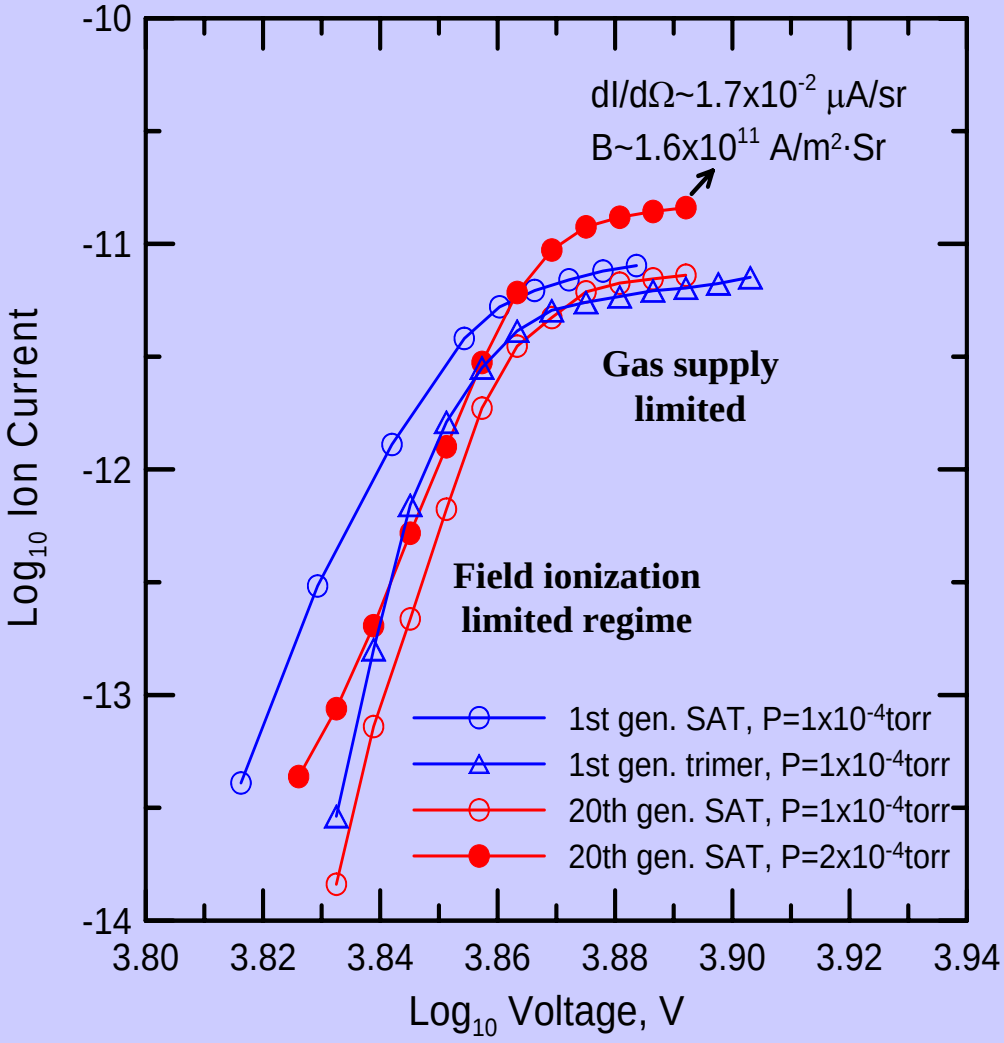


Fowler-Nordheim Plots



Field emission: extension angle ~ 6°
Field ionization: extension angle ~ 0.5°

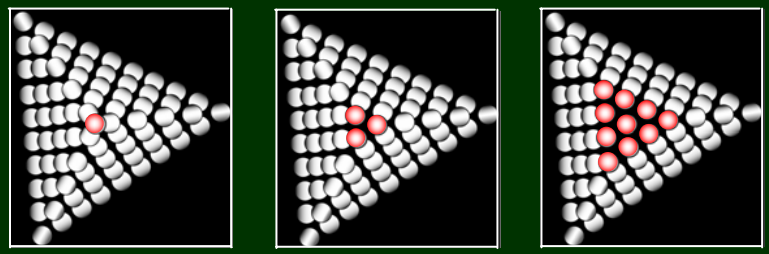
Rokuta & Oshima et al. '05
Kuo & Hwang et al. NANO Lett. '04

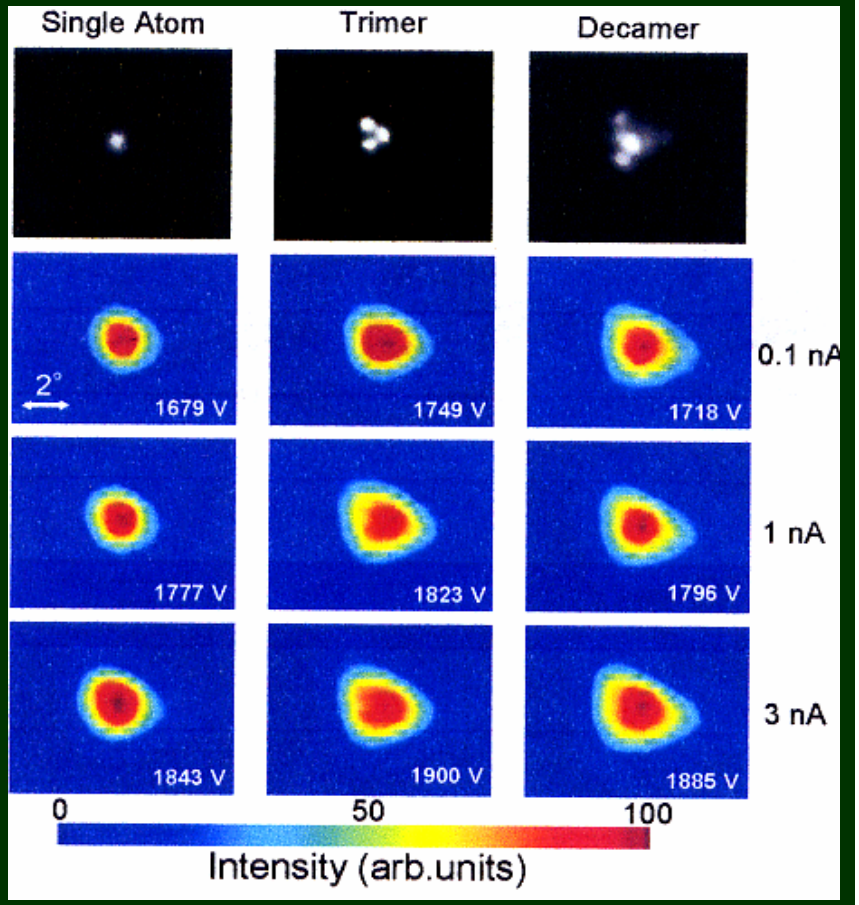


Kuo et al. '05

Ion source	α (degree)	dI/dΩ (μA/sr)	Source size (A^2)	B (A/m^2sr)
Plasma source	--	$3x10^3$		$\sim10^6$
GFIS H_2, 10^{-2} Torr	$\sim45^0$	~0.1	~100	$\sim10^{11}$
LMIS	$\sim30^0$	~20	$\sim2.5x10^5$	$\sim10^8$
SAT (This study at 10^{-4} Torr)	$\sim1^0$	~0.02	<10 (single atom)	$\sim10^{13}$

Possible use in Focused Ion Beam Source



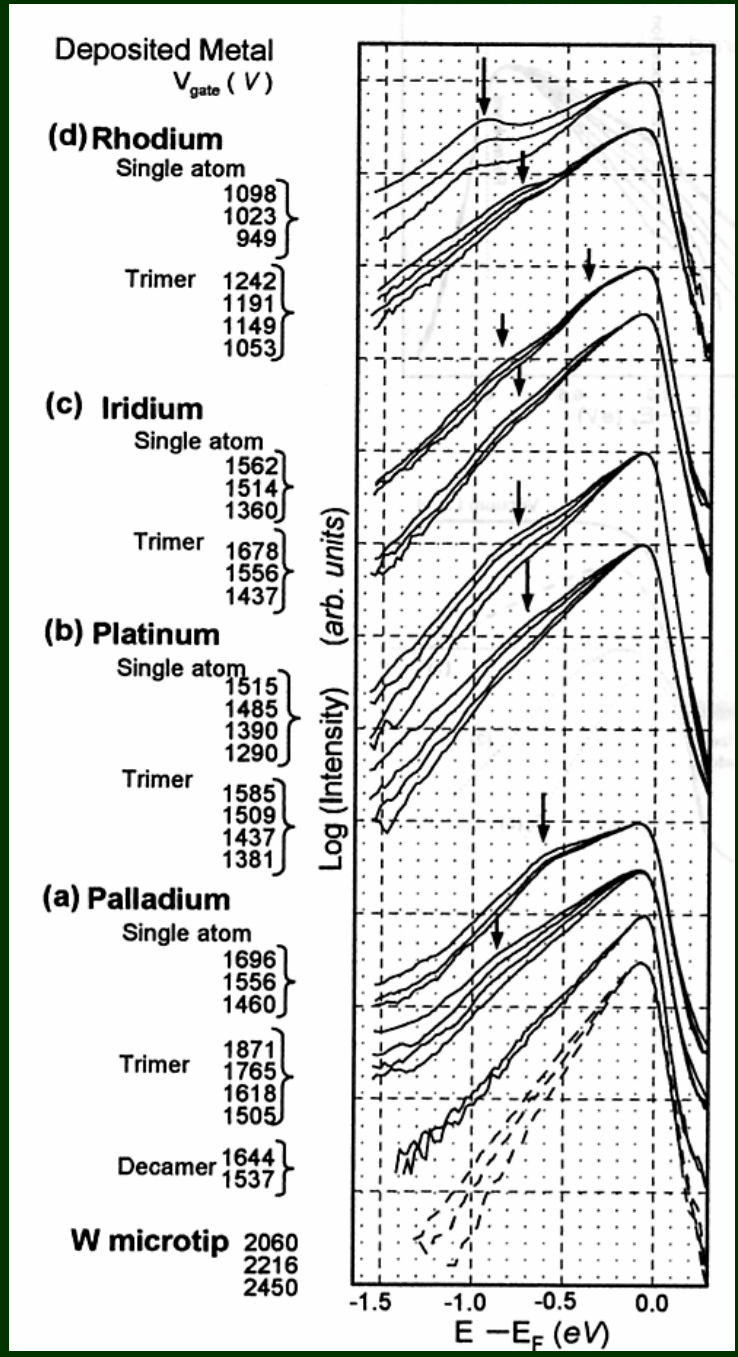


Ion image spot

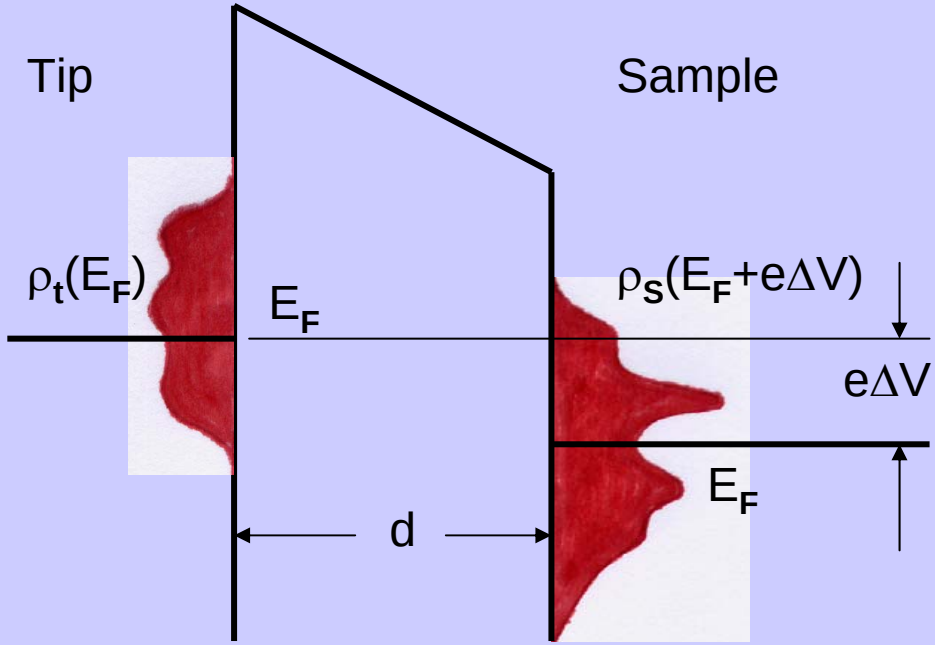
Electron image spot

Pd on W(111)

Rokuta et al. '06



Electronic Density of States Mapping of a Surface Using a Thermally & Chemically Stable Tip of Known Apex Atom can Provide a Chemical Map of Surface Atoms



Even if they are not, detailed structure of ρ_S may still help identify the chemical species of surface atoms.

$$I \propto \int_0^{eV} \rho_t(E_F-\varepsilon)\rho_S(E_F-eV+\varepsilon)T(d,eV)d\varepsilon$$

Tersoff & Hamann '83

If ρ_t is a δ-function, or $T(d,e\Delta V)$ are nearly constant:

$$\frac{dI}{dV} \propto \rho_S(E_F - eV)$$

Thanks to my many Coworkers:

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C. Oshima, E. Rokuta and colleagues

Thanks for Your Listening!

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