2018年11月12-14日　名古屋大学工学研究科・工学部
応用物理学特論・応用物理学特別講義（集中講義）

『表面物理学とトポロジカル物質への応用』

Lecture Slides (PDF files)
http://www-surface.phys.s.u-tokyo.ac.jp/KougiOHP/

東京大学理学系研究科物理学専攻
長谷川 修司

1. Nanoscience and Surface Physics ナノサイエンスと表面物理
   Nanoscience in Nobel Prize
2. Atomic Arrangements at Surfaces 表面原子配列構造
   Scanning Tunneling Microscopy, Electron Diffraction
   走査トンネル顕微鏡、電子回折
3. Surface Electronic States 表面電子状態
   Surface states 表面状態、 Rashba Effect ラシュバ効果
   Topological Surface States トポロジカル表面状態、
   Band Bending バンド湾曲
4. Surface Electronic Transport 表面電気伝導
   Space-Charge-Layer Transport and Surface-State Transport
   空間電荷層伝導と表面状態伝導
   Atomic-Layer Superconductivity　原子層超伝導

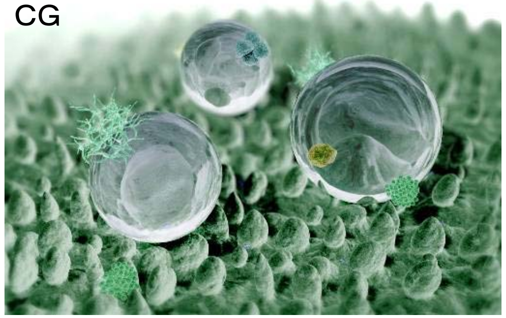
The Surface is Cool!

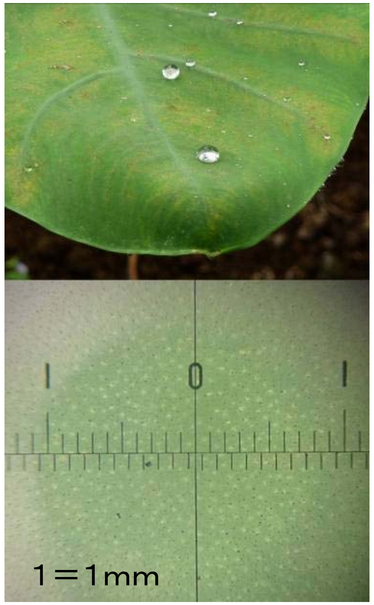
ロータス効果(Lotus effect, ハス効果)

天然の自浄機構（超撥水性 Ultrahydrophobicity）：
ハスの葉はその微細構造と表面の化学的特性により、濡れない。葉の表面についた水は表面張力によって丸まって水滴となり、泥や、小さい昆虫や、その他の異物を絡め取りながら転がり落ちる。（Wikipedia）

疎水性　hydrophobic
親水性　hydrophilic

CG



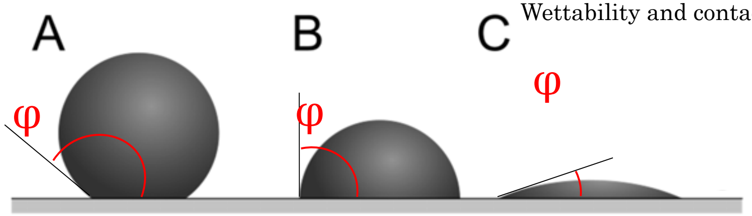


表面張力　Surface Tension (N/m)
表面の端の単位長さ当たりに生じる、縮もうとする力
Force, trying to shrink, per unit length at the edge of surface

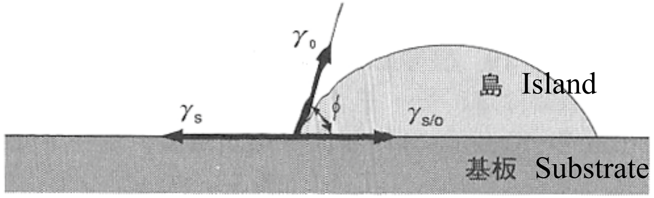
表面エネルギー Surface Energy (J/m^2)
単位面積の表面を作り出すのに必要なエネルギー
Energy necessary to create surface of unit area

←原子・分子間の引力 Attractive force among atoms and molecules

濡れと接触角
Wettability and contact angle



表面張力のつりあい Surface tension and Balance



Young(-Dupre) Formula

$$\boxed{\gamma_s = \gamma_{s/o} + \gamma_0 \cos\phi}$$

γ_s :基板表面の表面エネルギー（張力） Surface energy (tension) of Substrate

γ_0 :吸着物の表面エネルギー（張力） Surface energy (tension) of adsorbate

$\gamma_{S/0}$:基板と吸着物の界面エネルギー Interface energy between Substrate and adsorbate

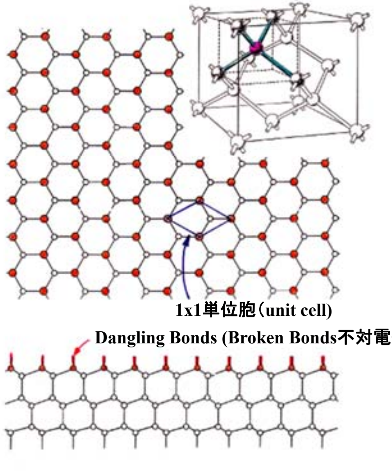
接触角 Contact angle φ

φ=0°	:wetting	φ～0°	:親水性 hydrophilic
φ>0°	:dewetting	φ> 90°	:疎水性 hydrophobic

Si(111)結晶表面 Crystal Surface

1×1切断（理想）表面
1×1 Truncated (Ideal) Surface

diamond 構造の単位格子
Unit cell of diamond lattice

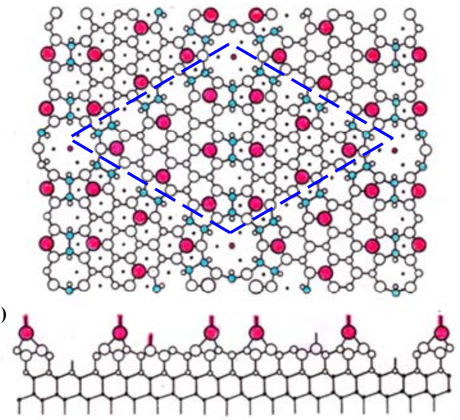


1x1単位胞（unit cell)

Dangling Bonds (Broken Bonds不対電子)

7×7表面超構造（最安定構造）
7×7 Surface Superstructure (most stable)

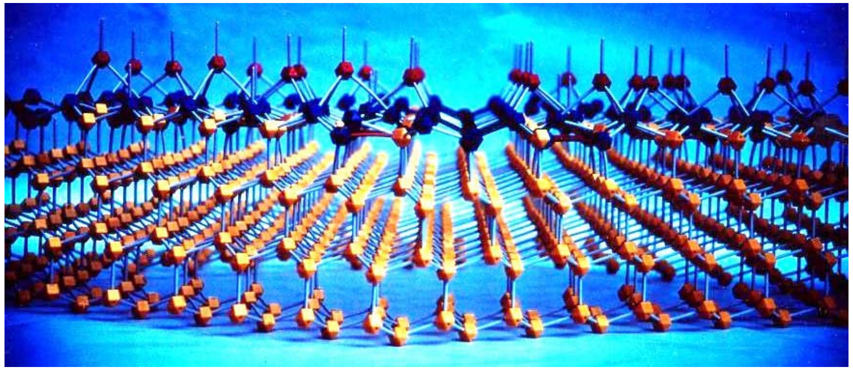
Decrease in number of dangling bonds（49→13）
→ Decrease in surface energy (stabilized）



高柳邦夫ら（東工大） Kunio Takayanagi (TIT) 1985

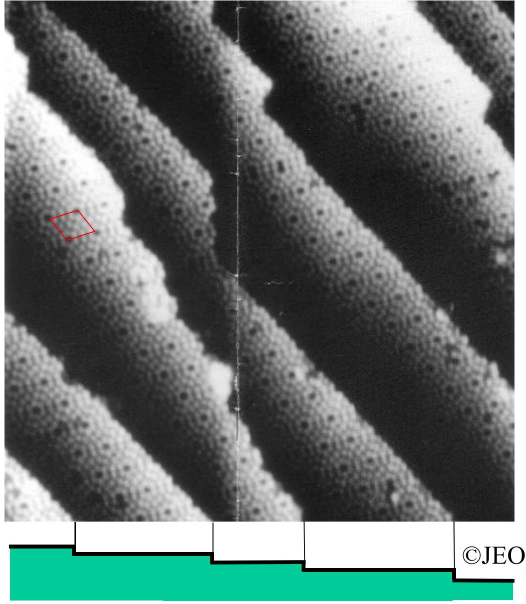
Si(111)-7×7清浄表面構造の模型

Ball-and-Stick Model of Si(111)-7×7 Clean Surface

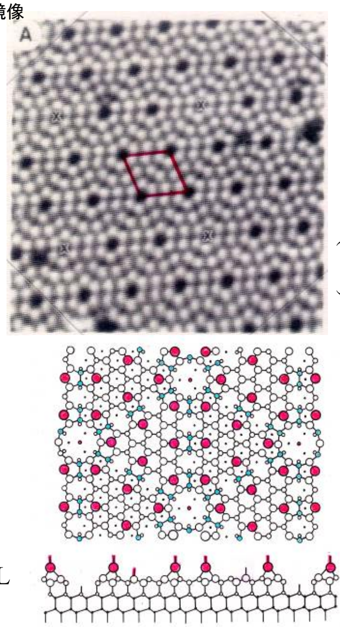


STM Image of Si(111)-7×7 Clean Surface

走査トンネル顕微鏡像



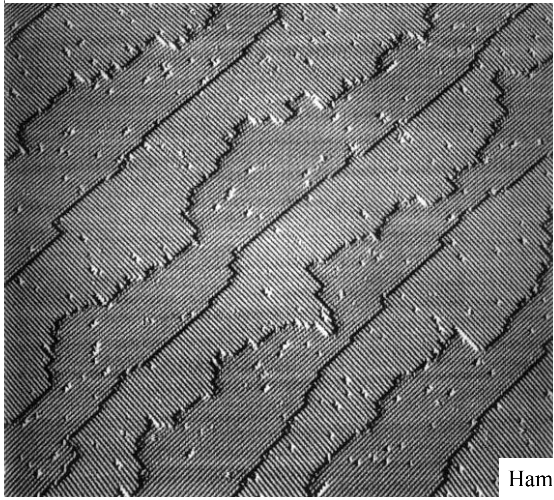
©JEOL

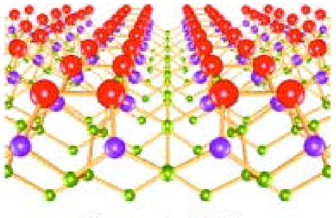


Pelz & Koch (IBM)

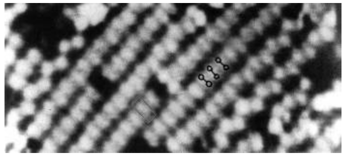
STM Image of Si(001)-2×1 清浄表面 Clean Surface

Swartzentruber, et al., Phys. Rev. Lett. 65 (1988) 1973



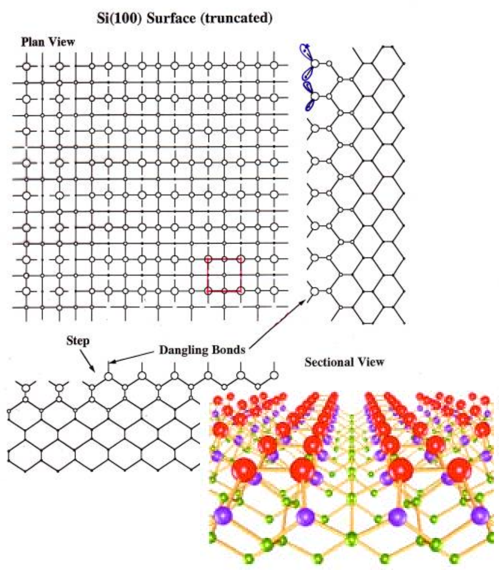


Symmetric Dimer

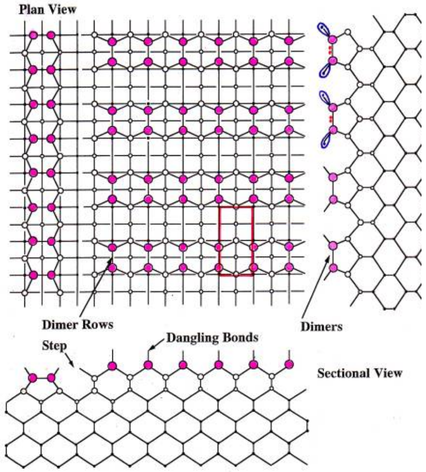


Hamers, et al., Phys. Rev. B34 (1986) 5343

Atomic Structure of Si(001)-2×1 Clean Surface

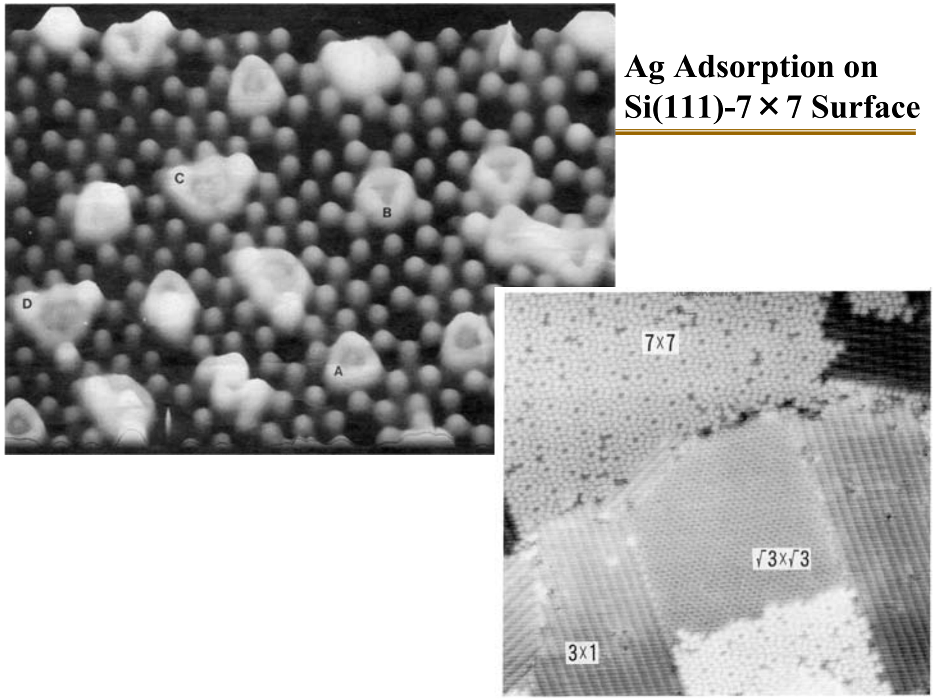


Symmetric Dimer

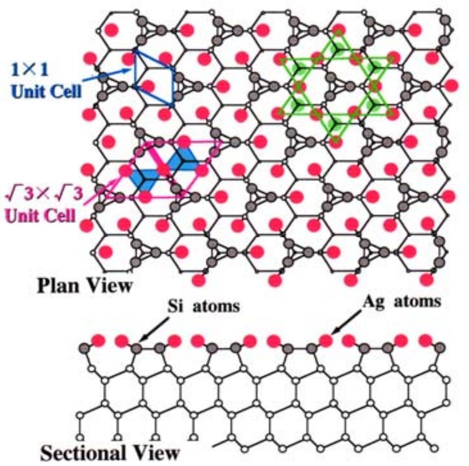


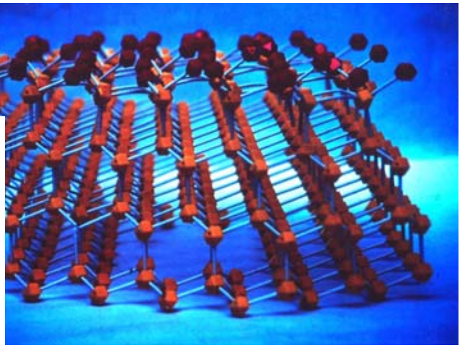
ダイマー(dimer)の形成
⇒ﾀﾞﾝｸﾞﾘﾝｸﾞﾎﾞﾝﾄﾞの減少
⇒表面エネルギーの低下(安定化)

Ag Adsorption on Si(111)-7×7 Surface



Si(111)-√3×√3-Ag 表面超構造 Surface Superstructure



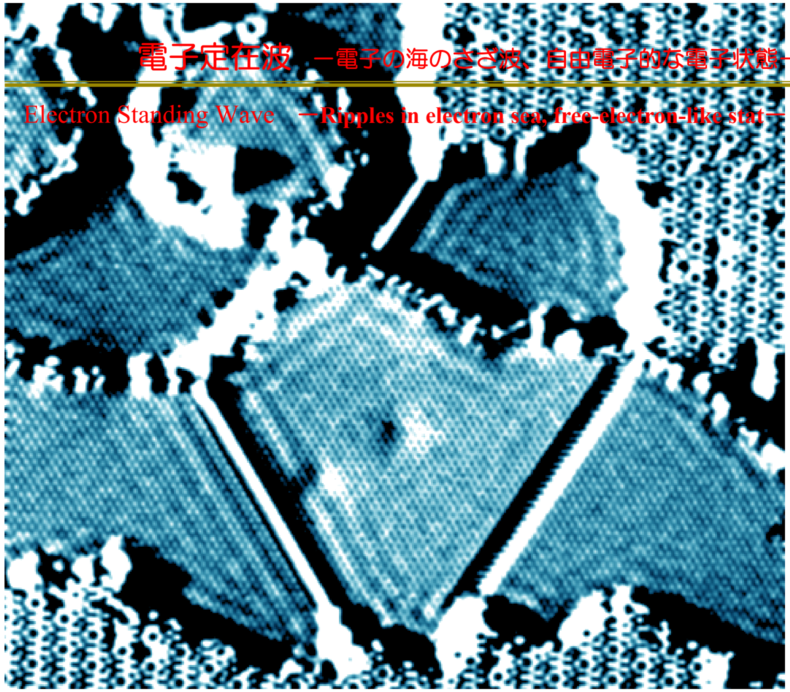


Honeycomb-Chained Triangle (HCT) Structre
高橋敏男ら(物性研) Toshio Takahashi (ISSP)

- **ダングリング・ボンド無し No dangling bonds**
- **原子的に平坦 Atomically flat**
- **2次元金属　Two-dimensional metal**

電子定在波 ー電子の海のさざ波、自由電子的な電子状態ー

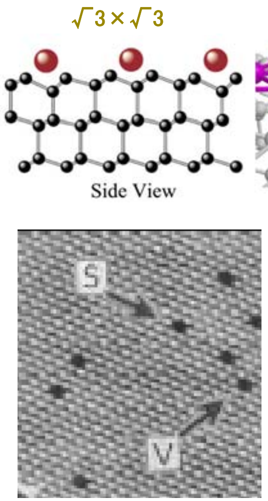
Electron Standing Wave ーRipples in electron sea, free-electron-like statー



N. Sato, et al., Phys. Rev. B 59, 2035 (1999).

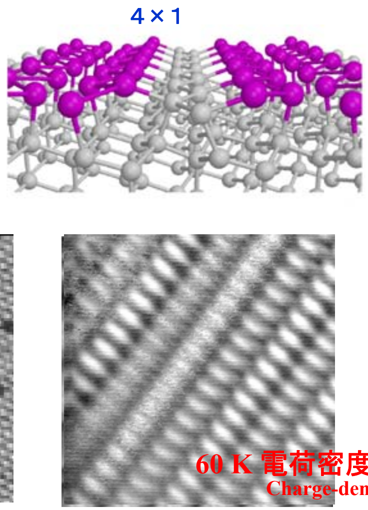
インジウム吸着Si(111) 表面 Indium-adsorbed Si(111) surfaces

絶縁体 Insulator



A. A. Sarranin, et. al.

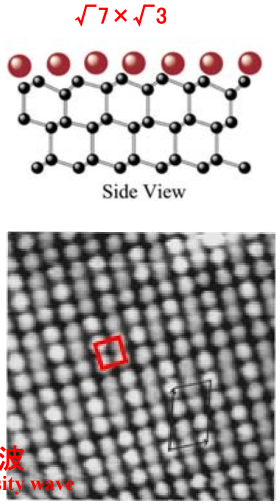
擬1次元金属 Quasi-1D Metal



60 K 電荷密度波
Charge-density wave

H. Y. Yeom, et al., PRL **82**, 4898 (1999)

2次元金属 2D Metal



S. L. Surnev, et. al.

電子回折

Electron Diffraction

電子の波長 Wavelength of Electron

- では電子の波長は？ How long is the wavelength of electron?

de Broglie's formula

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \sqrt{\frac{150.412}{V[\text{ボルト}]}}\ (\text{非相対論})$$

$$eV = \frac{p^2}{2m}$$

$$= \sqrt{\frac{150.412}{V[\text{ボルト}]}} \times (1 - 4.89 \times 10^{-7} \times V)\ (\text{相対論})$$

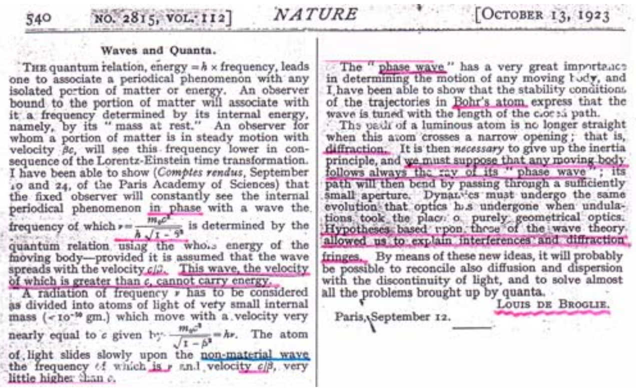
加速電圧 Acc. Voltage	λ（非相対論）	λ（相対論）
100 V	1.23 Å	1.23 Å
500 V	0.548 Å	0.548 Å
1 kV	0.388 Å	0.388 Å
5 kV	0.173 Å	0.173 Å
10 kV	0.123 Å	0.122 Å
50 kV	0.0548 Å	0.0535 Å
100 kV	0.0388 Å	0.0369 Å
500 kV	0.0173 Å	0.0131 Å

Atomic-Scale

電子の速度は光速に近い
The speed approaches c.

The Nobel Prize in Physics 1929

"for his discovery of the wave nature of electrons “ 電子の波動性に発見に対して



540 NO. 2815, VOL. 112] NATURE [OCTOBER 13, 1923

Waves and Quanta.

THE quantum relation, energy = h × frequency, leads one to associate a periodical phenomenon with any isolated portion of matter or energy. An observer bound to the portion of matter will associate with it a frequency determined by its internal energy, namely, by its "mass at rest." An observer for whom a portion of matter is in steady motion with velocity βc, will see this frequency lower in consequence of the Lorentz-Einstein time transformation. I have been able to show (*Comptes rendus*, September 10 and 24, of the Paris Academy of Sciences) that the fixed observer will constantly see the internal periodical phenomenon in phase with a wave the frequency of which $\nu = \frac{m_0c^2}{h\sqrt{1-\beta^2}}$ is determined by the quantum relation using the whole energy of the moving body—provided it is assumed that the wave spreads with the velocity c/β. This wave, the velocity of which is greater than c, cannot carry energy.

A radiation of frequency ν has to be considered as divided into atoms of light of very small internal mass ($< 10^{-50}$ gm.) which move with a velocity very nearly equal to c given by $\frac{m_0c^2}{\sqrt{1-\beta^2}} = h\nu$. The atom of light slides slowly upon the non-material wave the frequency of which is ν and velocity c/β, very little higher than c.

The "phase wave" has a very great importance in determining the motion of any moving body, and I have been able to show that the stability conditions of the trajectories in Bohr's atom express that the wave is tuned with the length of the closed path.

The path of a luminous atom is no longer straight when this atom crosses a narrow opening; that is, diffraction. It is then *necessary* to give up the inertia principle, and we must suppose that any moving body follows always the ray of its "phase wave"; its path will then bend by passing through a sufficiently small aperture. Dynamics must undergo the same evolution that optics has undergone when undulations took the place of purely geometrical optics. Hypotheses based upon those of the wave theory allowed us to explain interferences and diffraction fringes. By means of these new ideas, it will probably be possible to reconcile also diffusion and dispersion with the discontinuity of light, and to solve almost all the problems brought up by quanta.

LOUIS DE BROGLIE.

Paris, September 12.

Prince Louis-Victor Pierre Raymond de Broglie

France

Sorbonne University, Institut Henri Poincaré, Paris, France

b. 1892 d. 1987

運動する物体($V = c\beta$)には位相波を伴っている！ $mc^2 = h\nu$

non-material wave （⇒ material wave (物質波)）

光速より速く走る、エネルギーを運ばない $V_\phi = c/\beta$

$$\lambda = \frac{V_\phi}{\nu} = \frac{ch}{\beta mc^2} = \frac{h}{\beta mc} = \frac{h}{mV} = \frac{h}{p}$$

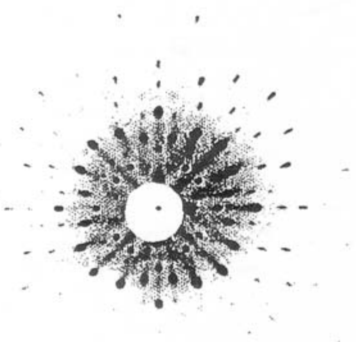
→ 干渉・回折縞を説明できる！

NaClのX線回折

→X線結晶構造解析

Laueの条件＝Braggの式

（～寺田寅彦）



NaClの四回対称面のラウエ写真

$$2d\sin\theta = n\lambda$$

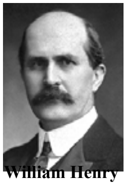
The Nobel Prize in Physics 1914

“for his discovery of the diffraction of X-rays by crystals”

Max von Laue
(1879-1960)

The Nobel Prize in Physics 1915

“for their services in the analysis of crystal structure by means of X-rays”



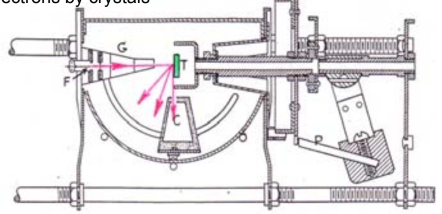
Sir William Henry Bragg
(1862-1942)

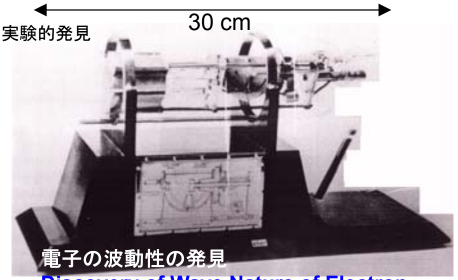
William Lawrence Bragg
(1890-1971)

First Electron Diffraction – Davisson & Germer — （LEED 75 eV）

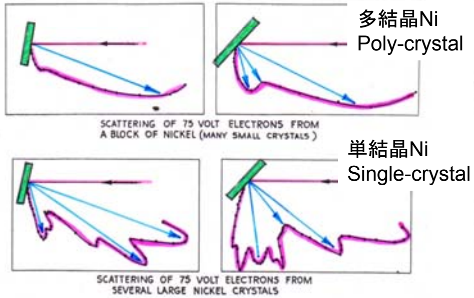
C. Davisson and L. H. Germer, Phys. Rev. 30, 705-740 (1927)

1937 Nobel Prize in Physics 結晶による電子の干渉現象の実験的発見
Experimental discovery of diffraction of electrons by crystals



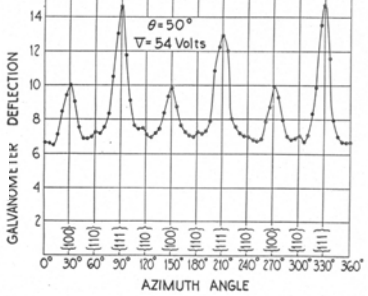


電子の波動性の発見
Discovery of Wave Nature of Electron



多結晶Ni
Poly-crystal

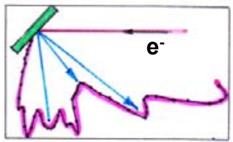
単結晶Ni
Single-crystal



The Nobel Prize in Physics 1937

"for their experimental discovery of the diffraction of electrons by crystals"

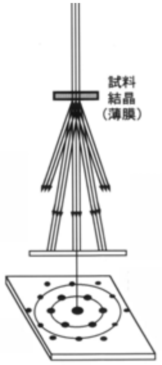
結晶による電子の回折の実験的発見

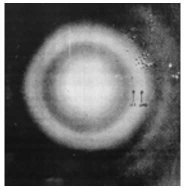


Ni Crystal : LEED

Clinton Joseph Davisson
USA
Bell Telephone Laboratories

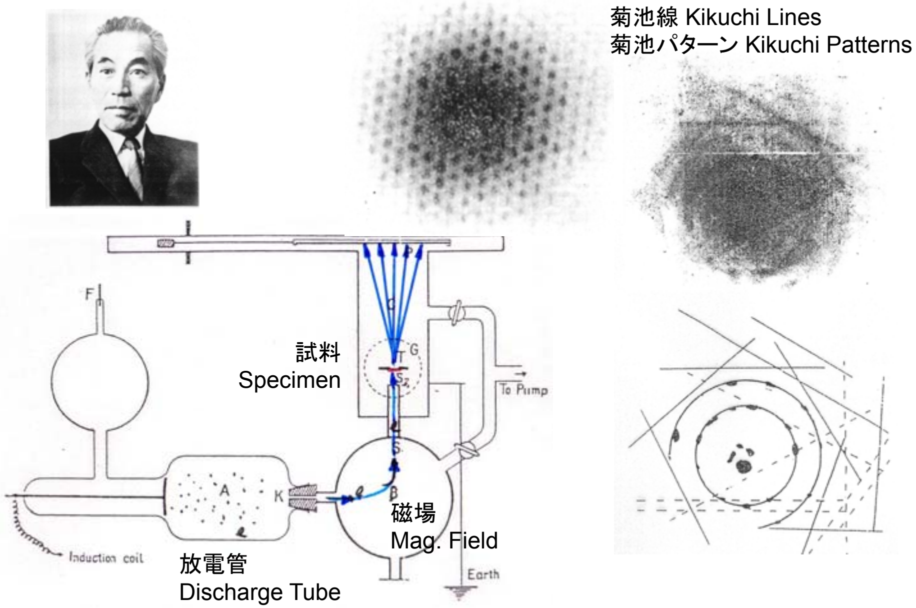
George Paget Thomson
Great Britain
London University





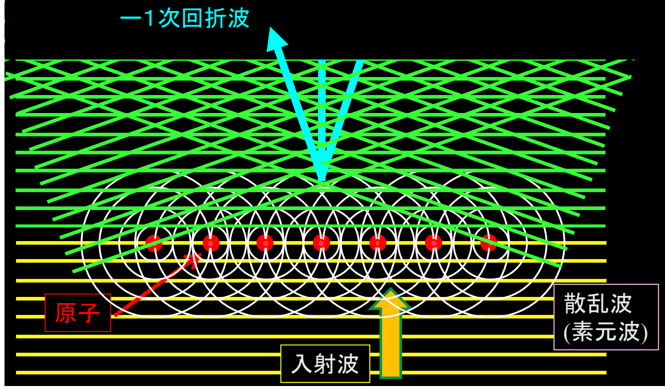
Au Thin Film :TED

菊池正士 の電子回折　ー雲母薄膜のTED ー
Electron Diffraction by Seishi Kikuchi ーTED of Mica Thin Film



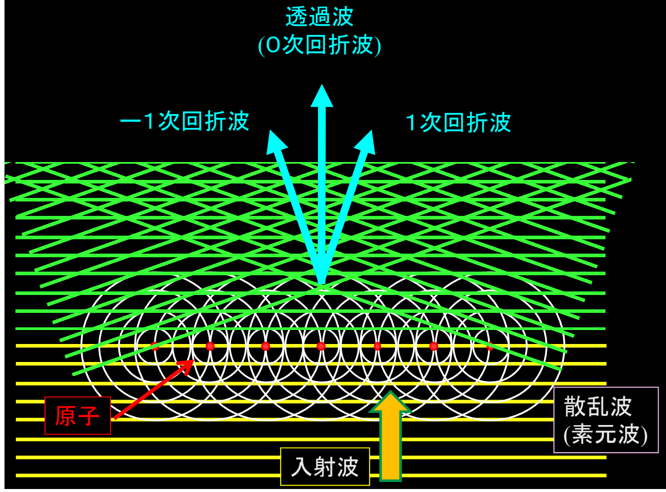
回折条件

Huygensの原理 ⇨ Laue条件＝Bragg条件

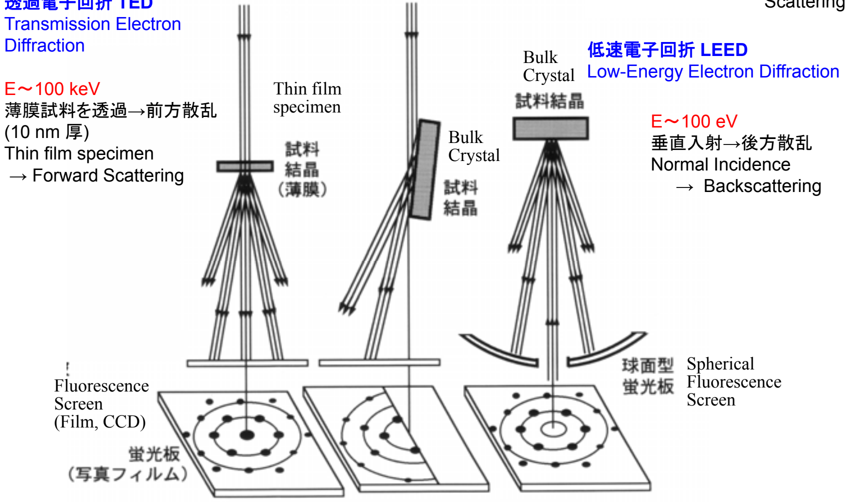


回折条件

Huygensの原理 ⇨ Laue条件＝Bragg条件



電子回折いろいろ Various Types of Electron Diffraction



透過電子回折 TED
Transmission Electron Diffraction

E～100 keV
薄膜試料を透過→前方散乱
(10 nm 厚)
Thin film specimen
→ Forward Scattering

反射高速電子回折 RHEED
Reflection-High-Energy Electron Diffraction

E～10 keV
かすりの角度入射→前方散乱
Grazing Incidence →Forward Scattering

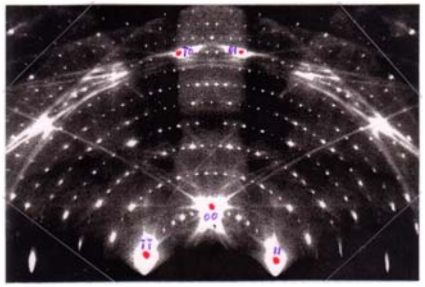
低速電子回折 LEED
Low-Energy Electron Diffraction

E～100 eV
垂直入射→後方散乱
Normal Incidence
→ Backscattering

Electron Diffraction Pattern from Si(111)-7×7 Clean Surface

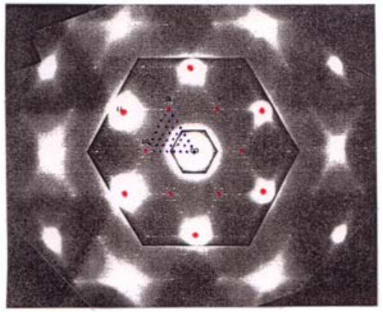
- 基本格子反射点
  Fundamental Spots
  (Diffraction spots from bulk crystal)

他の細かいスポット
超格子反射点
Superlattice Spots
(Diffraction spots from surface superstructure)

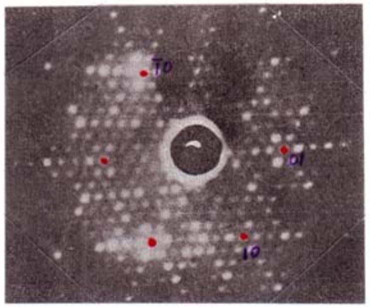


RHEED

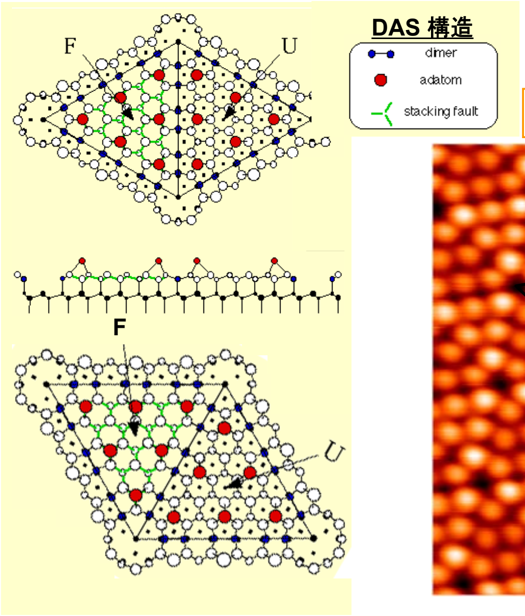
TED（Takayanagi）



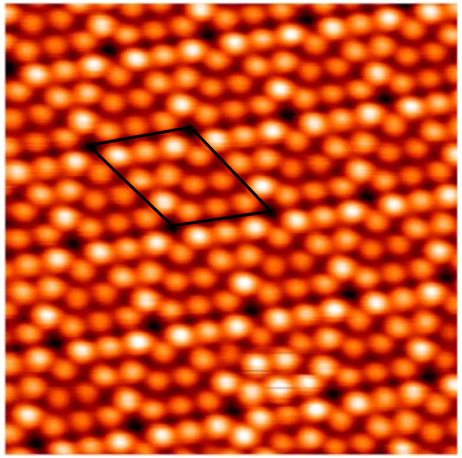
LEED（Ino）



固体表面

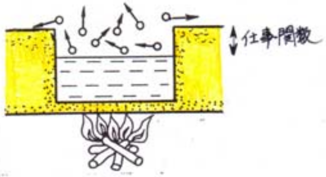


Si(111)7x7表面のSTM像

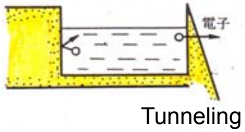


電子線源　— 熱電子銃と電界放射電子銃 —
Electron Beam Source –Thermal Electron Gun & Field-Emission Electron Gun-

熱電子銃 Thermal EG
（1901 Richardson）

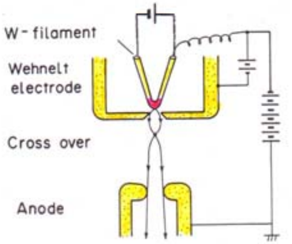


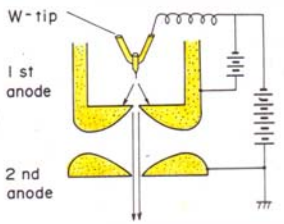
電界放射電子銃 Field-Emission EG
（1968 Crewe）



Tunneling

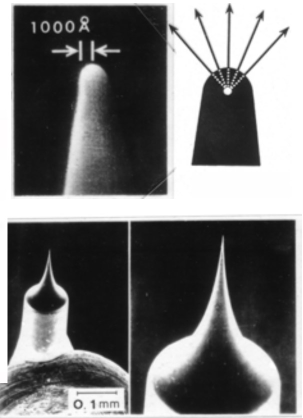
壁が10Å以下になると，電子は
トンネル効果で外に飛び出す．



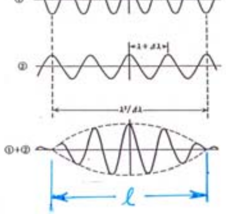


Field Emission Tip　(W)

仮想光源
Virtual Source
～ 100 Å



電子波束の大きさ Size of Electron Wave Packet



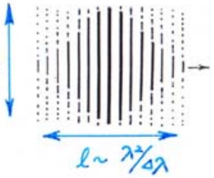
$\ell \sim \frac{\lambda^2}{\Delta\lambda}$

$$\left(\frac{1}{\lambda}-\frac{1}{\lambda+\Delta\lambda}\right)^{-1}=\frac{\lambda(\lambda+\Delta\lambda)}{\Delta\lambda}\cong\frac{\lambda^2}{\Delta\lambda}$$

Plane wave e^{ikz} is impossible in reality!

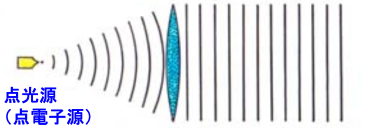
Transverse coherence length

$W \sim \frac{\lambda}{2\beta}$

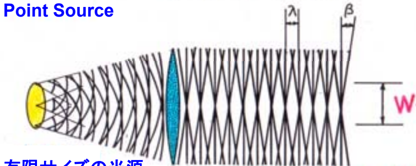


$\ell \sim \lambda^2/\Delta\lambda$

Longitudinal coherence length



点光源
（点電子源）
Point Source



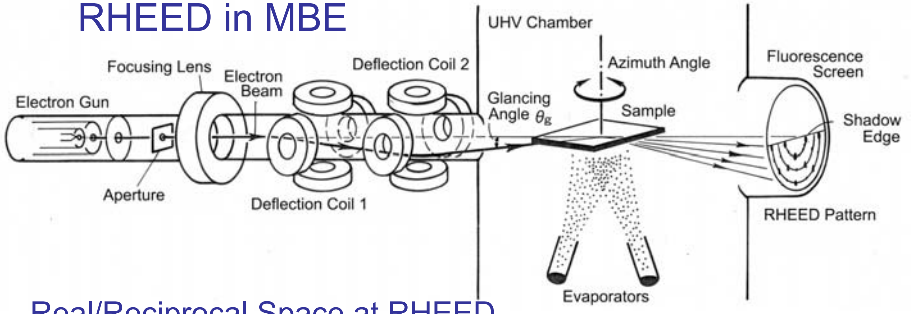
$W \sim \frac{\lambda}{2\beta}$

有限サイズの光源
（現実の電子源）
Finite-Size Source (in reality)

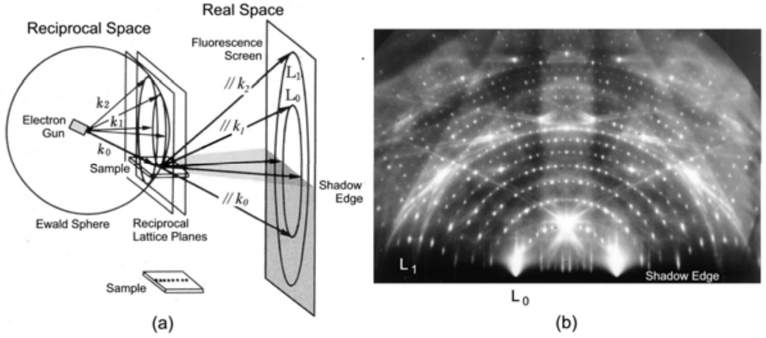
β：開き角
Divergence Angle

	熱電子銃（ヘアピン型）	電界放射電子銃（冷陰極型）
光源サイズ (μm)	～20	～0.01
エネルギー幅 (eV)	～ 2	～ 0.3
輝度 at 100 keV (A/cm^2/st)	～5×10^5	～5 ×10^8
波束		
長さ l (μm)	～ 0.2	～ 1.3
幅 W (μm)	～ 0.02	～ 0.6
(レンズで拡大)	2	60

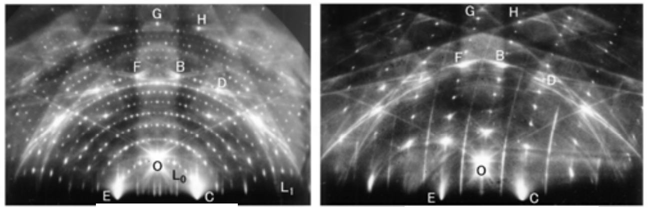
RHEED in MBE



Real/Reciprocal Space at RHEED

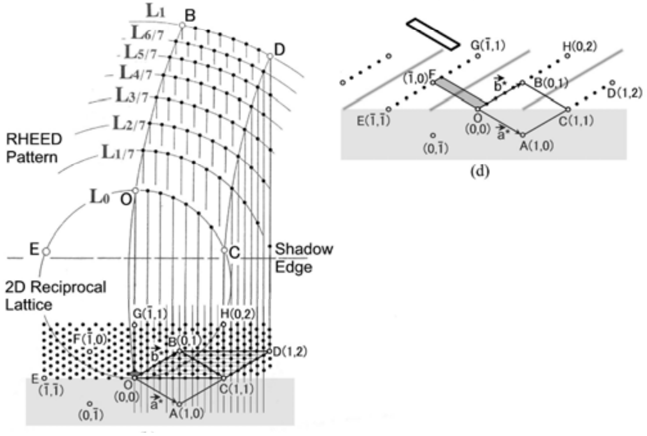


RHEED Patterns & 2D Reciprocal Lattice

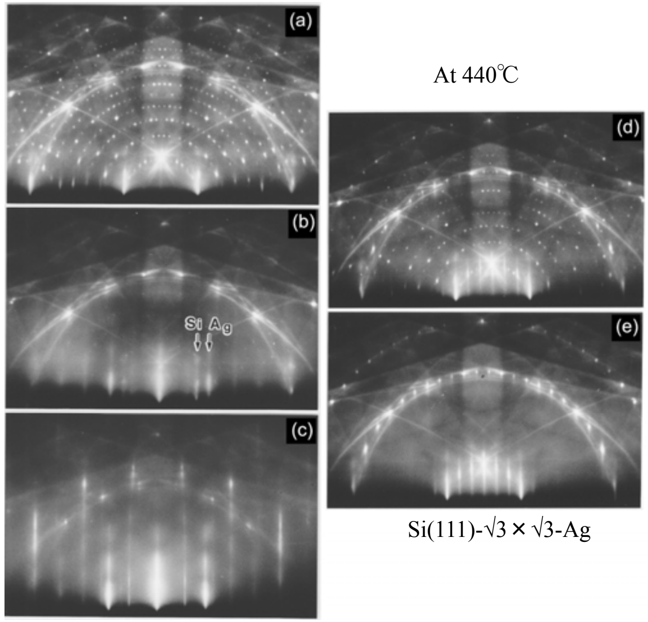


Si(111)-7 × 7

Si(111)-5 × ’2’-Au



Ag deposition on Si(111)-7 × 7



At RT

Ag=1.5 ML

Ag=3.0 ML

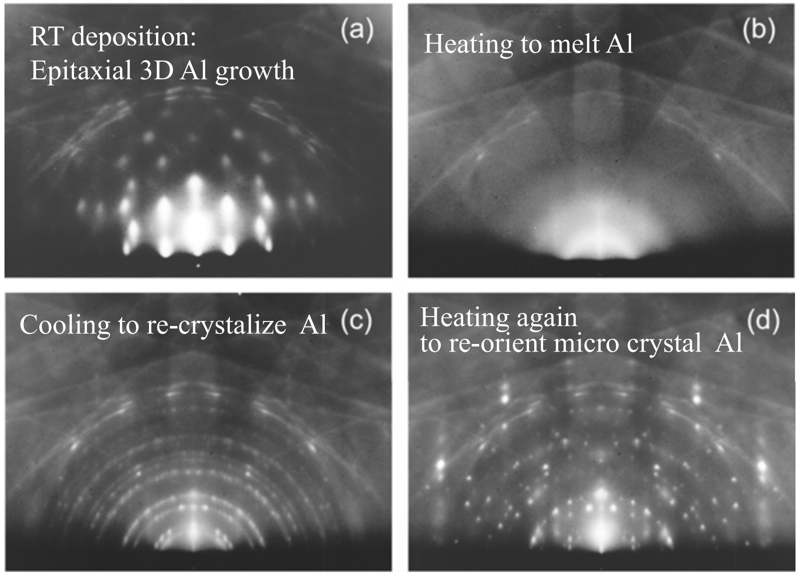
At 440℃

Ag=0.5 ML

Ag=1.0 ML

Si(111)-√3 × √3-Ag

Melting and Crystallization of Al (20 ML) on Si(111)-7 × 7



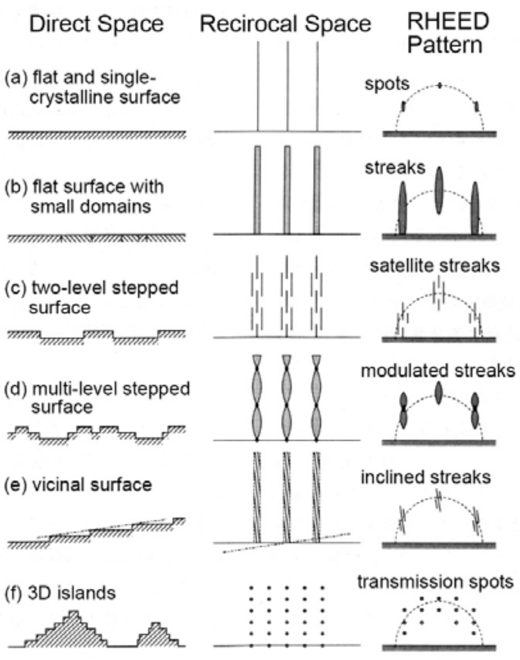
RT deposition:
Epitaxial 3D Al growth

Heating to melt Al

Cooling to re-crystalize Al

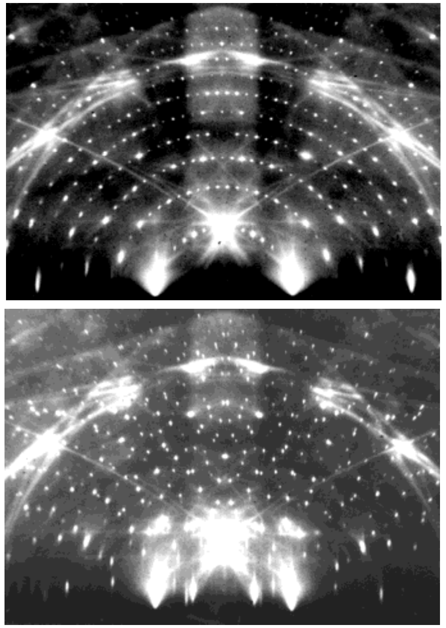
Heating again
to re-orient micro crystal Al

RHEED Patterns from various surfaces

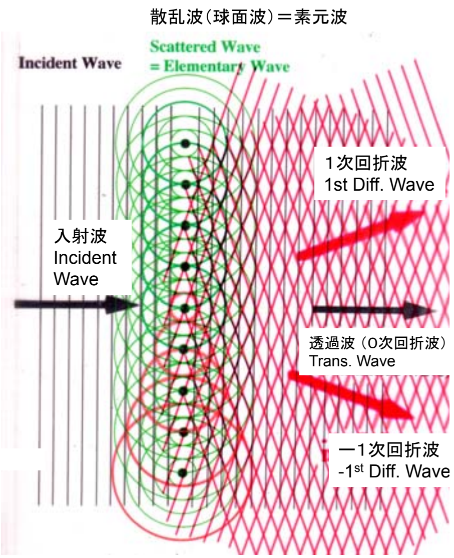


Courtesy by
Yoshimi Horio

回折スポットの並び方と強度：原子配列の解析



Huygens’ Principle & Diffraction



回折スポットの並び方と強度

１. 個々の原子からの散乱（素元波）
- ⇒原子散乱因子 Atomic Scattering Factor *f*
  原子の種類、価数

２. 単位胞内の原子からの散乱波の干渉
- ⇒結晶構造因子 Crystal Structure Factor *F*
  単位胞内での原子の具体的な配置
- ⇒各スポットの強度、消滅則

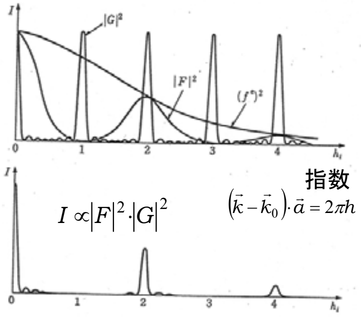
$$F=\sum_{i}^{\text{単位胞}} f_i\cdot\exp\left[-2\pi i\left(\vec{k}-\vec{k}_0\right)\cdot\vec{r}_i\right]$$

３. 結晶全体（単位胞の繰り返し）からの散乱
- ⇒ラウエ関数 Laue Function *G*
  単位胞の大きさ・形（構造の周期）、
  結晶・ドメインの大きさ、形状
- ⇒各スポットの並び方（回折波の方向）

$$G=\frac{\sin\left[\frac{1}{2}N\left(\vec{k}-\vec{k}_0\right)\cdot\vec{a}\right]}{\sin\left[\frac{1}{2}\left(\vec{k}-\vec{k}_0\right)\cdot\vec{a}\right]}$$

各スポットの強度

$$I\propto|F|^2\cdot|G|^2\propto|F|^2$$



$$I\propto|F|^2\cdot|G|^2$$

指数

$$\left(\vec{k}-\vec{k}_0\right)\cdot\vec{a}=2\pi h$$

Procedure of Structure Analysis: Trial and Error

(1) **Measure the intensity** $I\left(\vec{k}\right)$ **of each diffraction spot**

(2) **Assume a model of the atomic arrangement in the unit cell.**

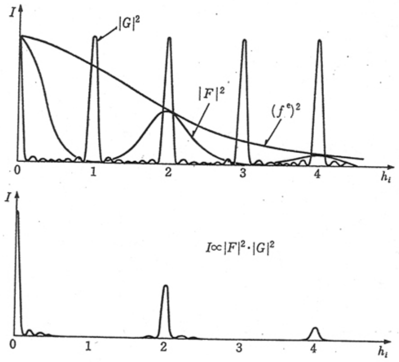
(3) **Calculate the potential** $V\left(\vec{r}\right)$ **from the model.**

(4) **Fourier transform the** $V\left(\vec{r}\right)$ **to obtain the crystal structure factor** $F\left(\vec{k}\right)$ **.**

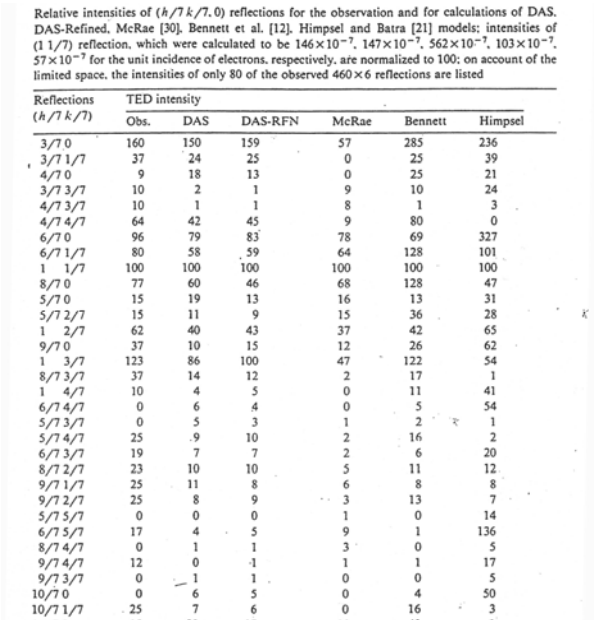
(5) **Compare the calculated** $\left|F\left(\vec{k}\right)\right|^2$ **with the measured spot intensity** $I\left(\vec{k}\right)$ **.**

(6) **If they do not agree with each other, modify the model, and repeat the process (2)-(5) until a satisfactory agreement.**

$$I\propto|F|^2\cdot|G|^2\propto|F|^2$$

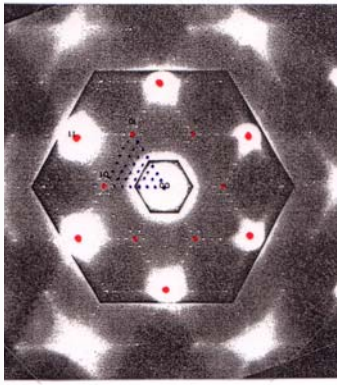


TED Analysis of Si(111)-7x7 Surface Superstructure by Takayanagi etal.
—Proposal of DAS Structure —



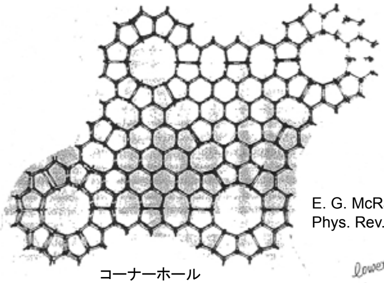
Relative intensities of ($h/7\,k/7.0$) reflections for the observation and for calculations of DAS. DAS-Refined, McRae [30], Bennett et al. [12], Himpsel and Batra [21] models; intensities of ($1\,1/7$) reflection, which were calculated to be 146×10^{-7}, 147×10^{-7}, 562×10^{-7}, 103×10^{-7}, 57×10^{-7} for the unit incidence of electrons, respectively, are normalized to 100; on account of the limited space, the intensities of only 80 of the observed 460×6 reflections are listed

Reflections ($h/7\,k/7$)	TED intensity					
	Obs.	DAS	DAS-RFN	McRae	Bennett	Himpsel
3/7 0	160	150	159	57	285	236
3/7 1/7	37	24	25	0	25	39
4/7 0	9	18	13	0	25	21
3/7 3/7	10	2	1	9	10	24
4/7 3/7	10	1	1	8	1	3
4/7 4/7	64	42	45	9	80	0
6/7 0	96	79	83	78	69	327
6/7 1/7	80	58	59	64	128	101
1 1/7	100	100	100	100	100	100
8/7 0	77	60	46	68	128	47
5/7 0	15	19	13	16	13	31
5/7 2/7	15	11	9	15	36	28
1 2/7	62	40	43	37	42	65
9/7 0	37	10	15	12	26	62
1 3/7	123	86	100	47	122	54
8/7 3/7	37	14	12	2	17	1
1 4/7	10	4	5	0	11	41
6/7 4/7	0	6	4	0	5	54
5/7 3/7	0	5	3	1	2	1
5/7 4/7	25	9	10	2	16	2
6/7 3/7	19	7	7	2	6	20
8/7 2/7	23	10	10	5	11	12
9/7 1/7	25	11	8	6	8	8
9/7 2/7	25	8	9	3	13	7
5/7 5/7	0	0	0	1	0	14
6/7 5/7	17	4	5	9	1	136
8/7 4/7	0	1	1	3	0	5
9/7 4/7	12	0	1	1	1	17
9/7 3/7	0	1	1	0	0	5
10/7 0	0	6	5	0	4	50
10/7 1/7	25	7	6	0	16	3



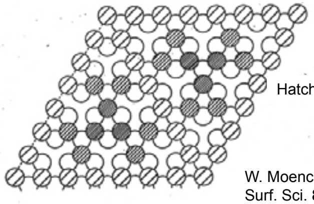
K. Takayanagi, et al.,
Surf. Sci. **164**, 367 (1985).

Proposed Models for Si(111)-7x7 Surface Superstructure



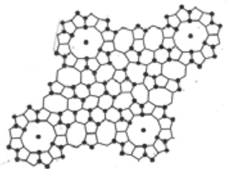
コーナーホール
ダイマー

E. G. McRae,
Phys. Rev. B **28**, 2305 (1983).



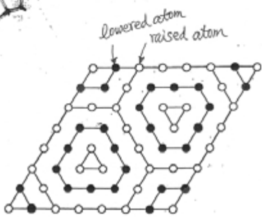
Hatched atoms; raised atoms

W. Moench,
Surf. Sci. **86**, 672 (1979).

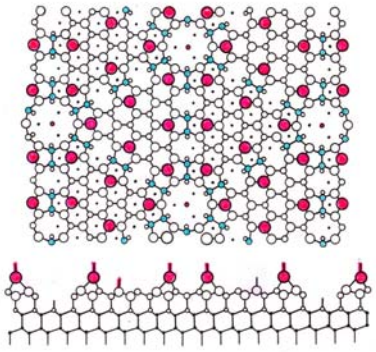


コーナーホール
ダイマー、非対称な半単位胞

F. J. Himpsel,
Phys. Rev. B **27**, 7782 (1983).

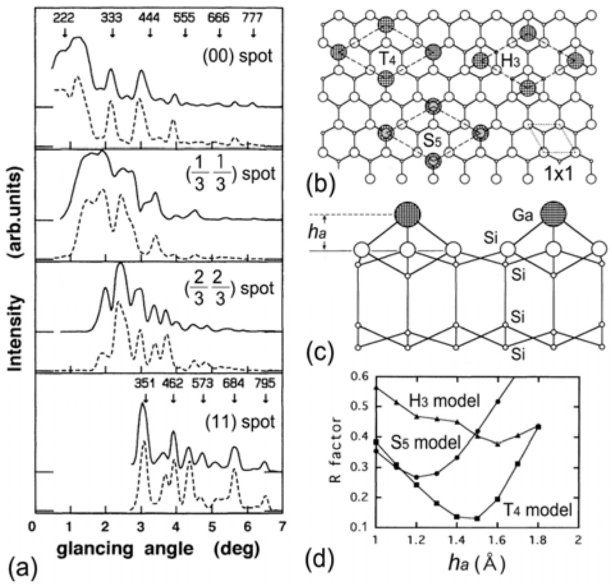


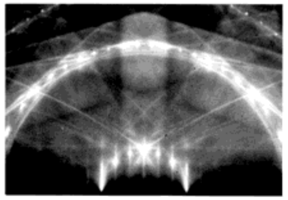
D. J. Chadi,
Surf. Sci. **99**, 1 (1980).



K. Takayanagi, et al., Surf. Sci. **164**, 367 (1985).

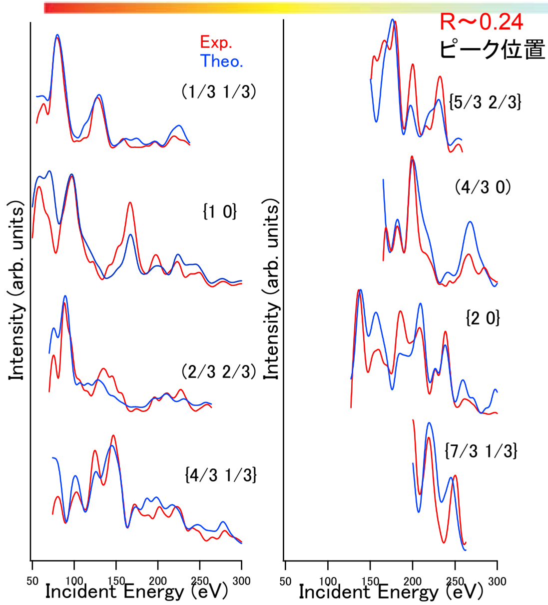
Rocking RHEEDによる構造解析：Si(111)-√3×√3-Ga





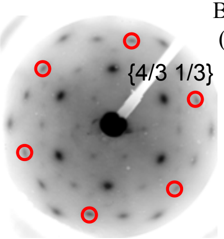
Hanada, T., Daimon, H.,
and Ino, S: Phys. Rev.
B **51**:13320 (1993).

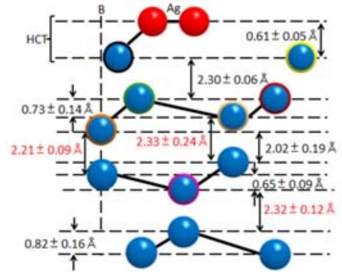
I-V LEEDによる構造解析：silicene



R～0.24
ピーク位置と強度がよく一致

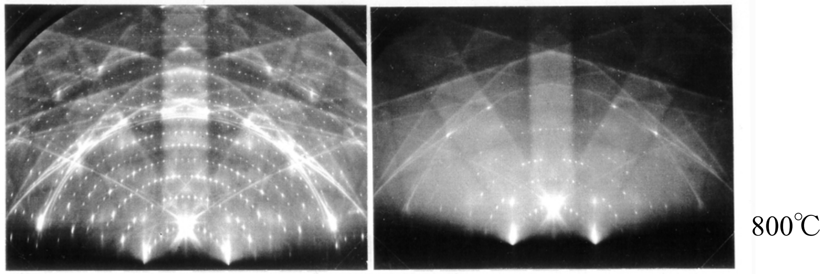
T. Shirai, et al.,
Phys. Rev.
B **89**, 241403(R)
(2014)

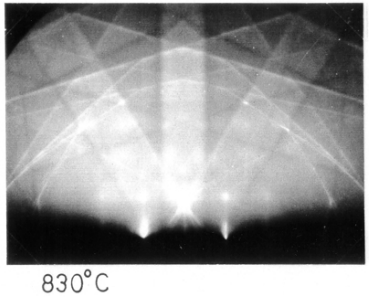


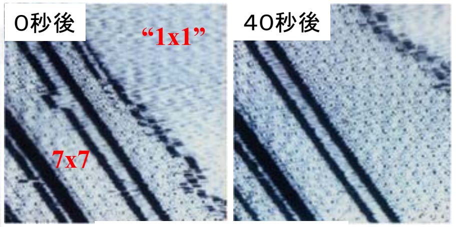


Si(111)-7x7 ⇔ 1x1 相転移 at ～830℃

S. Ino: JJAP **16**, 891 (1977)



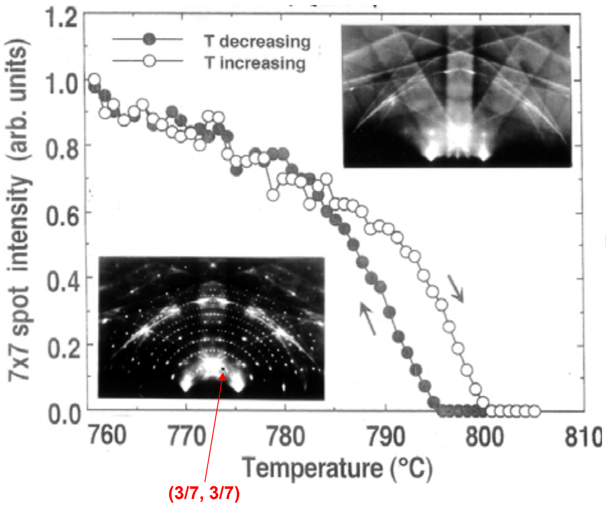




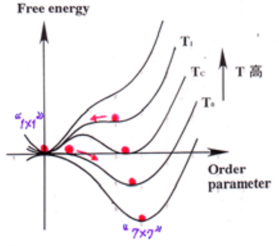
864℃でのSTM像

S. Kitamura *et al*., Nature **351**, 215 (1991).
K. Miki *et al*., Ultramicroscopy **42-44**, 851 (1992).

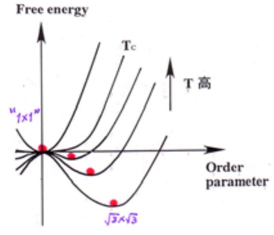
Si(111)-7x7 ⇔ 1x1 相転移 ; 1次相転移



S. Hasegawa, et al., Phys. Rev. B **47**, 9903 (1993).
Phase Transitions **53**, 87 (1995).

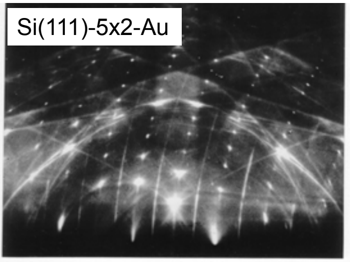


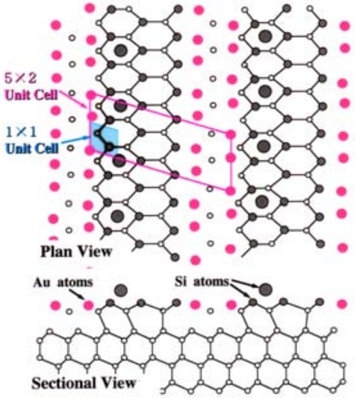
1 次相転移
Order parameter の不連続的な変化
温度ヒステリシス



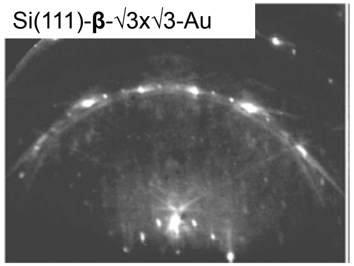
2 次相転移
Order parameter の連続的な変化
温度ヒステリシス無し

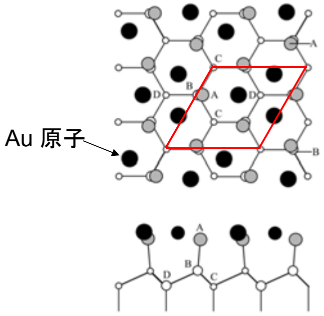
Au-吸着表面超構造 on Si(111)





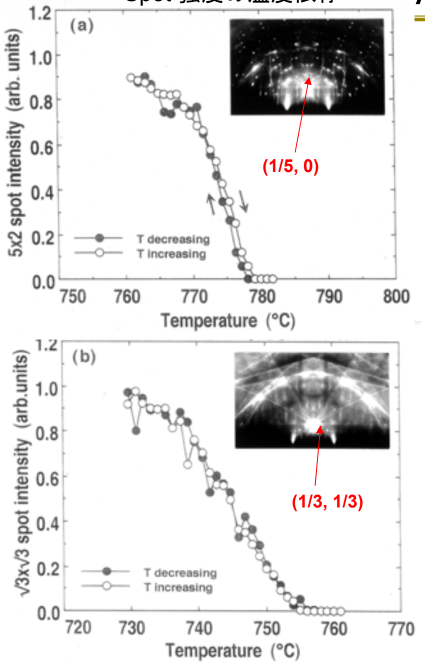
Marks & Plass, PRL **75**, 2172 (1995).



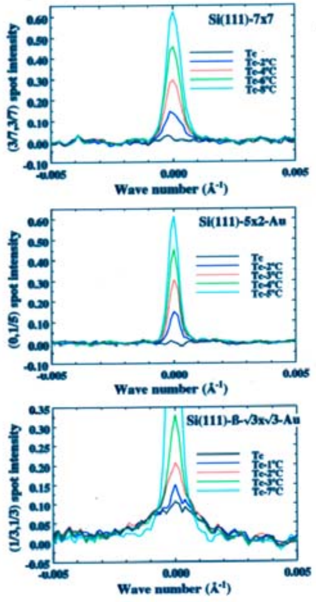


Au-吸着表面超構造 on Si(111)の相転移

Spot 強度の温度依存



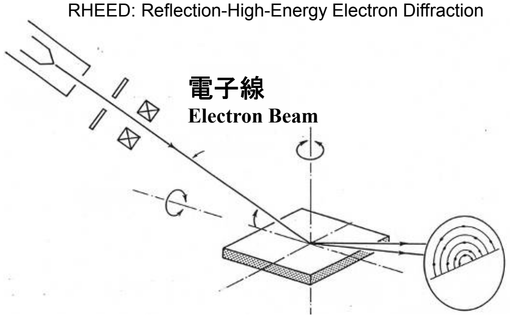
Spot Profileの温度依存



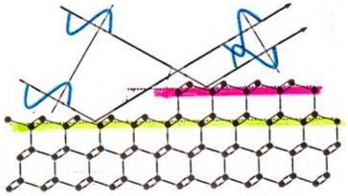
Atomic-Layer Growth and RHEED Intensity Oscillation

Harris, Joyce, Dobson 1981

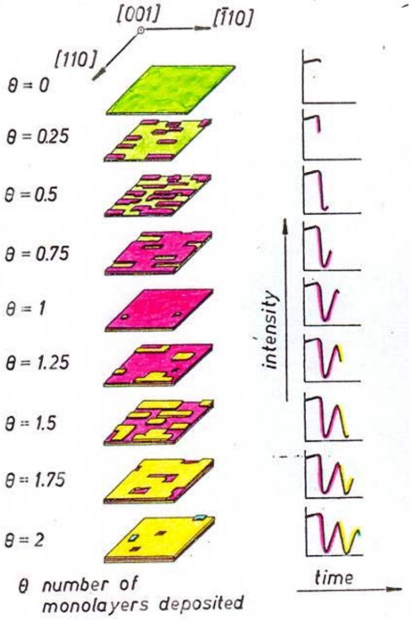
RHEED: Reflection-High-Energy Electron Diffraction



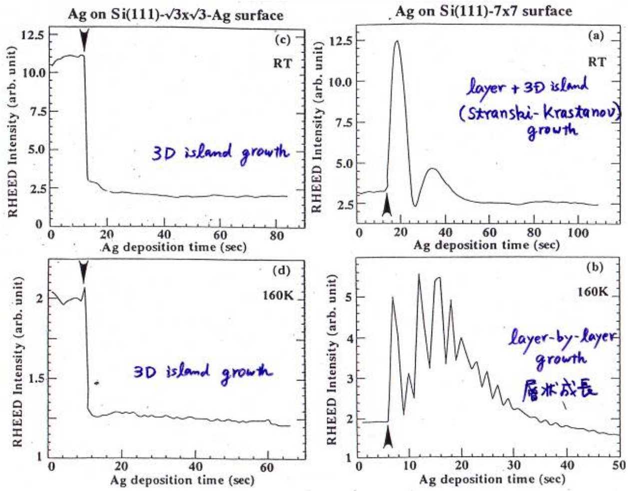
Off-Bragg Condition (Out-of-Phase Condition)



Layer-by-layer Growth

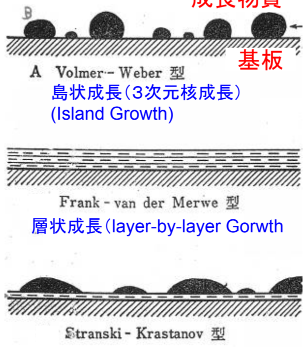


Atomic-Layer Growth and RHEED Intensity Oscillation



成長物質

基板



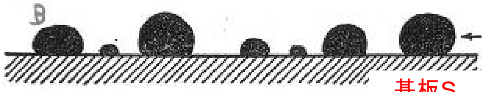
島状成長（3次元核成長）
(Island Growth)

層状成長（layer-by-layer Gorwth

混合成長 (Mixed Grwoth)

原子層・薄膜の成長モード Growth Modes

成長物質A



基板S

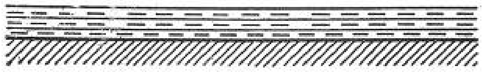
A Volmer－Weber **Mode**

dewetting

島状成長（3次元核成長、island (3D Nucli) Growth

$\gamma_S < \gamma_A$ 格子不整合 Lattice Mismatch

γ_S: **Surface Energy of Substrate**
γ_A: **Surface Energy of Adsorbate**



Frank－van der Merwe **Mode**

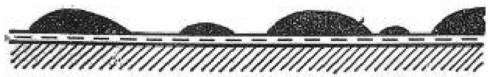
層状成長（layer-by-layer Grwoth）

wetting

$\gamma_S > \gamma_A$ 格子整合 Lattice Match

Governing Factor

- 表面(界面)エネルギー
  Surface(Interface) Energy
- 格子不整合による
  歪みエネルギー
  Strain Energy due to
  Lattice Mismatch



Stranski－Krastanov **Mode**

混合成長 Mixed Growth　格子不整合 Lattice Mismatch

wetting→dewetting

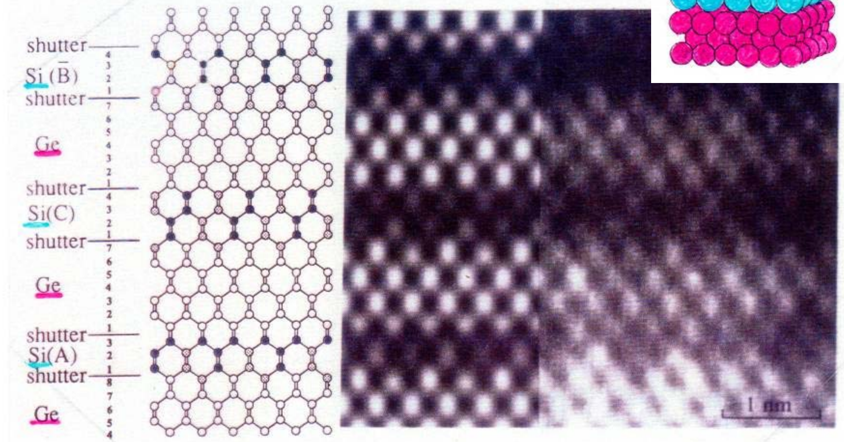
$\gamma_S > \gamma_A \Rightarrow \gamma_S' < \gamma_A$

γ_S': **吸着層の表面エネルギー**
Surface Energy of Adlayer

超格子構造 – 人工結晶
Superlattice Structures—Man-made Crystal

異なる原子を積み重ねる
→ 自然には存在しない人工物質
（量子井戸）

Stack up different atoms layer-by-layer
⇒ Artificial materials which do not exist in nature.
(Quantum well structures)



GeSi超格子の電子顕微鏡写真 TEM image of GeSi superlattice

The Nobel Prize in Physics 2007

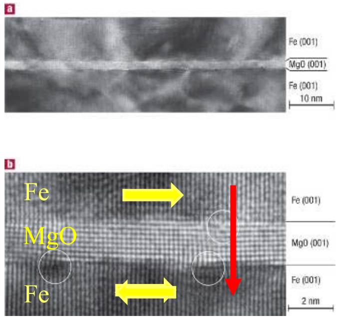
巨大磁気抵抗効果の発見
for the discovery of Giant Magnetoresistance"
——→ 磁気ヘッド（ハードディスクの小型化・高密度化）
Magnetic head (down sizing and high-density magnetic hard disk)

Albert Fert
France
南パリ大学

b. 1938

Peter Grünberg
Germany
Julich研究所

b. 1939



S. Yuasa, et al., Nature Materials 3, 868 (2004).

トンネル磁気抵抗効果**(TMR)**
Tunnel magnetoresistance
Parallel M ⇒ Low resistance
Anti-parallel M ⇒High resistance

The Nobel Prize in Physics 2014

明るく省エネの白色光源を可能にした、
効率的な青色発光ダイオードの発明
for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources

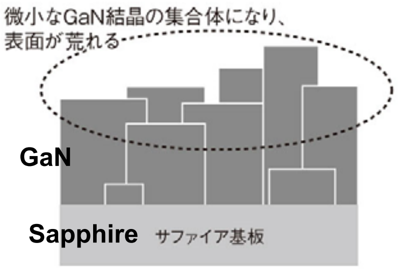
赤﨑 勇終身教授
（名城大学）
85歳

天野 浩教授
（名古屋大学）
54歳

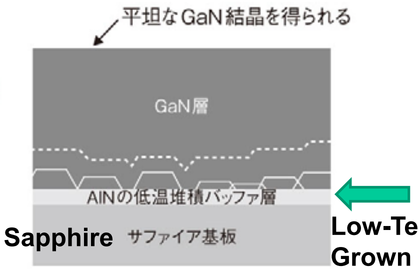
中村 修二教授
（カリフォルニア大学）
60歳

Growth of GaN Crystal：Low-Temp. Buffer Layer
GaN 窒化ガリウム

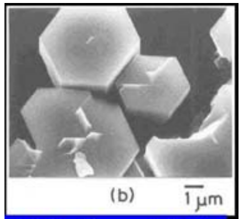
Without Buffer Layer
(a)バッファ層を導入しない場合



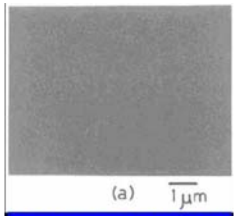
With Buffer Layer
(b)バッファ層を導入した場合



Low-Temp. Grown AlN Layer



低温バッファ層なし



低温バッファ層あり

Release Strain in GaN

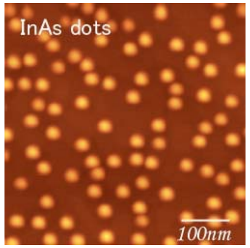
（財）武田計測先端知財団
2005／7／21

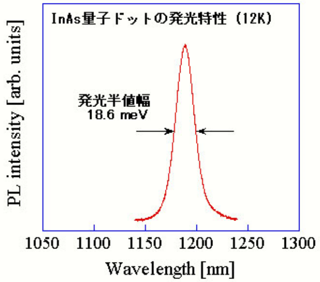
SK成長を利用した量子ドットの自己組織的形成

Self-Organization of Quantum Dots due to Stranski-Krastanov Growth

電気通信大学 ECU　山口浩一研究室 Prof. K. Yamaguchi

InAs/GaAs





Photoluminescence Spectrum

格子不整合（格子不整合量, 7.2%）のため、FvMモードからVWモードへ
20 nm程度の小さいピラミッド状のInAs微小結晶粒が約1兆個/cm^2
電子（または正孔）がInAsドット内に閉じ込められ、量子サイズ効果
ドットサイズを制御⇒発光波長を制御できる（量子ドットレーザ）

まとめ　電子回折 Summary Electron Diffraction

１. 量子力学の基礎：電子の波動性の実証

Fundamentals of Quantum Mechanics; Wave Nature of E

２. 表面構造の定性的な観察

Qualitative Analysis of Surface Structures

試料準備に有用 Useful for sample prep

３. 表面原子配列の精密解析

Detailed analysis of surface atomic arrangement

運動学的計算⇒動力学的計算

Kinematical ⇒ Dynamical Claculations

４. 動的構造変化のモニター

Monitor of dynamical changes in structure

- 原子層成長 growth of atomic layers
- 相転移 phase transitions