2018年11月12-14日　名古屋大学工学研究科・工学部

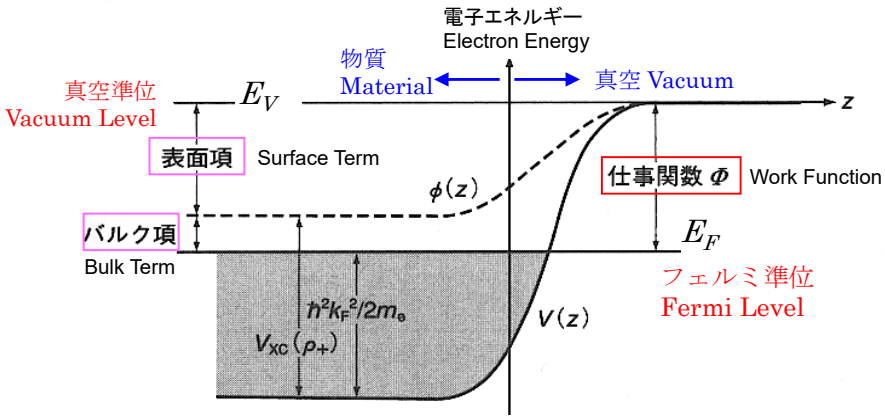
応用物理学特論・応用物理学特別講義（集中講義）

東京大学理学系研究科物理学専攻
長谷川 修司

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

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

エネルギーダイヤグラムと仕事関数　Energy Diagram & Work Function

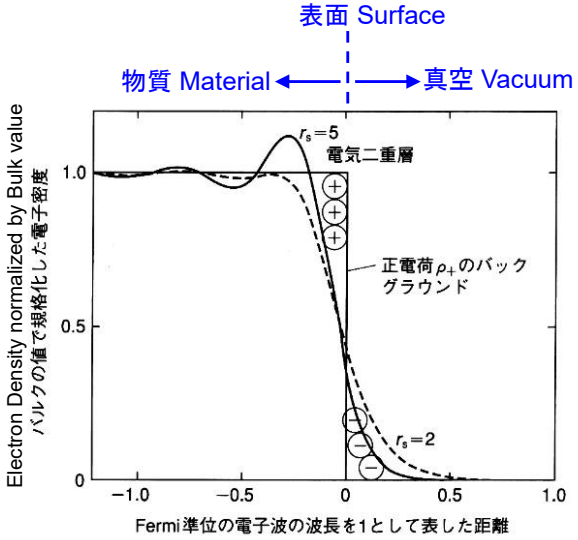


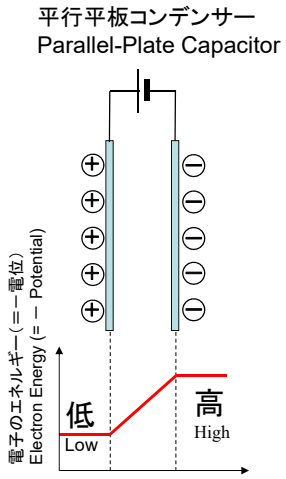
- 物質中の電子を外に取り出すのに必要なエネルギーの最小値
  The minimum energy necessary for taking an electron out of the material
- 物質中の最高占有エネルギー準位にある電子を真空準位に上げるのに必要なエネルギー
  The energy necessary to excite an electron at the highest occupied level to the vacuum level

「物質の外」: 無限遠ではなく、物質の表面の直上（表面から鏡像力の影響を無視できる程度の距離 ～1 μm）の真空中
Outside of the Material = a position away from the surface (～1 μm) at which the image force is ignored, not a position at infinite.

表面項 Surface Term

電子の滲みだしと表面電気二重層　Spill out of electrons & Surface Electric Dipole Layer





バルク項（交換相関エネルギーV_{XC})-(運動エネルギー)

Bulk Term (Exchange-Correlation Energy V_{XC})-(Kinetic Energy)

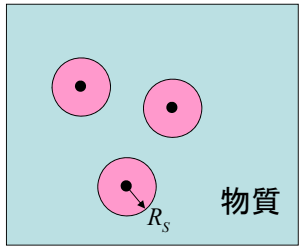
それぞれの電子の周りには電子密度の低い領域（正電荷を帯びた領域）が存在　⇒真空中の電子に比べて安定化（エネルギーが下がる V_{XC}）
Low-el-density area (positively charged area) around each electron　⇒ Each electron is more stabilized than that in vacuum (Energy lowering V_{XC})

クーロン孔，相関ホール (Correlation Hole)

電子間のクーロン反発によって他の電子を遠ざけている
（相関相互作用）(Correlation Inter. due to Coulomb repulsion)

フェルミ孔，交換ホール (Exchange Hole)

同じスピンを持つ電子どうしは，パウリの排他原理による
交換相互作用による反発がはたらき他の電子を遠ざけている
(Exchange Inter. due to Paul's Exclusion Principle)



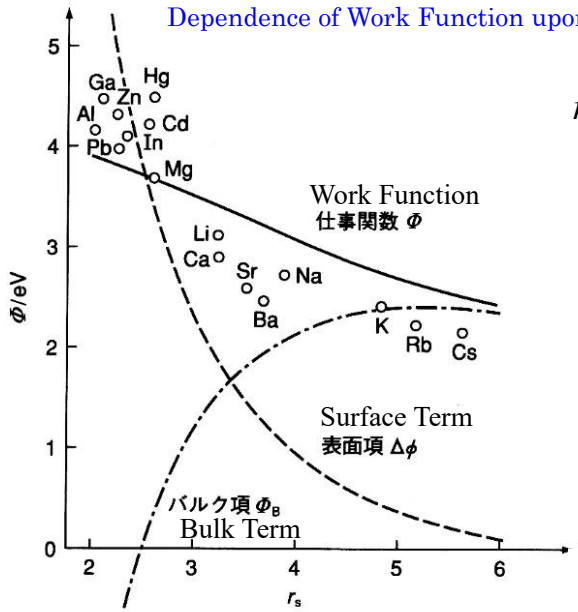
ρ: 電子の数密度（個/cm³）Number density of electrons (1/cm³)

$\frac{4\pi}{3}R_S^3$: 1個の電子が占める体積（cm³）Volume occupied by an electron (cm³)

$$\rho = \frac{1}{\left(\frac{4\pi}{3}R_S^3\right)} \Rightarrow R_S = \left(\frac{3}{4\pi\rho}\right)^{1/3} \overset{\text{無次元化 Dimensionless}}{\Rightarrow} r_S = \frac{(3/4\pi\rho)^{1/3}}{a_B}$$

a_B : Bohr Radium (0.52 Å)

仕事関数の電子密度依存性
Dependence of Work Function upon Electron Density



$$r_S = \frac{(3/4\pi\rho)^{1/3}}{a_B}$$

r_S : 大きい Large
⇒低電子密度 Low Density
⇒バルク項の寄与大
Bulk Term: Large
表面項の寄与が小
Surface Term : Small

r_S : 小さい Small
⇒高電子密度High Density
⇒バルク項の寄与小
Bulk Term: Small
表面項の寄与大
Surface Term: Large

金属単結晶の仕事関数 Work Function of Metal Single Crystal

結晶構造 Crystal Structure	金属 Metal	面方位 Face Orientation (100)	(110)	(111)
bcc	K	1.65	1.78	1.85
	Fe	4.67	5.05	4.81
	Mo	4.53	4.95	4.55
fcc	Al	4.20	4.28	4.24
	Ni	5.22	5.04	5.35
	Cu	4.59	4.48	4.94
	Ag	4.64	4.52	4.74
	Ir	5.67	5.42	5.76
	Au	5.22	5.20	5.26

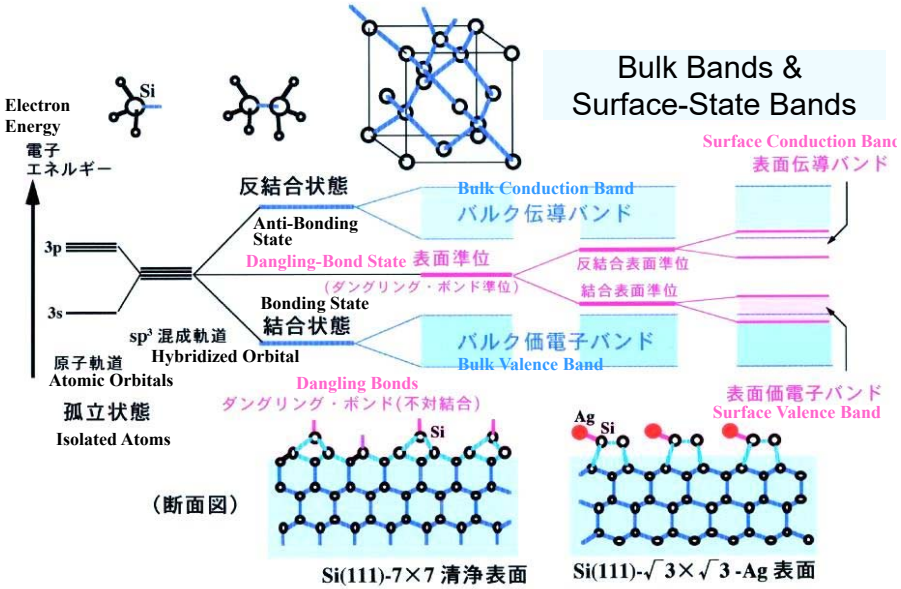
a) 単位は eV とした. In unit of eV

表面項が違う:原子数の表面密度が大きいほど表面二重電気層が強くなり、仕事関数が大きくなる。
Different Surface Term: As larger the atom density at surface is, stronger the surf. Electric Dipole Layer is. ⇒ larger Work Function

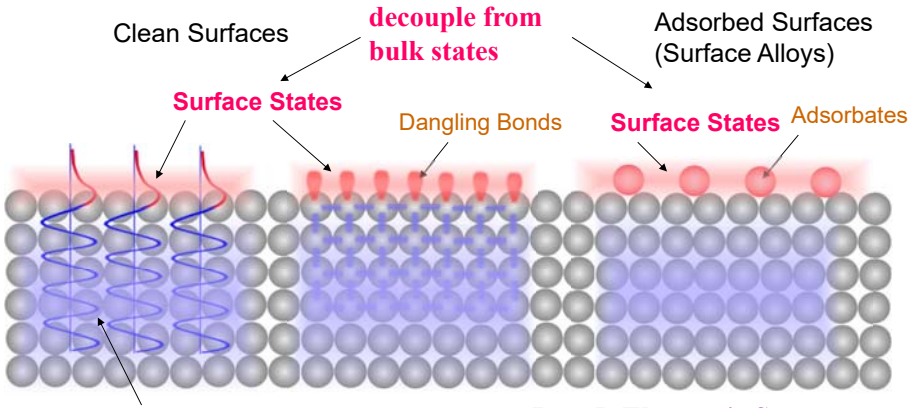
fcc金属 : (111)>(100)>(110)
bcc金属 : (110)>(111)>(100)

電子を物質から取り出して無限遠にもっていくのに必要なエネルギーは、取り出す結晶面によらずに同じ。

From Energy Levels to Band Formation



Surface States — Shockley & Tamm States —



-Low-D Electronic Systems
-Broken (Space-Inv.) Symmetry
-New Periodicity

⇔ Topological surface states

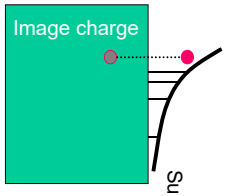
Various Surface States

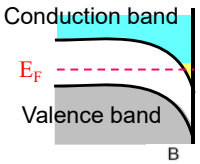
1. Shockley states (extended)
   Tamm states (localized)
   Chemical bonding,
   Surface Potential

2. Image states
   Image charge

3. Surface space-charge layer
   Bending of bulk bands

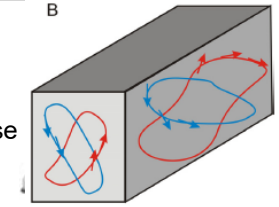
4. Topological surface states
   Spin-orbit coupling ← Edge states of Q(S)H phase
   HgTe (QW), $Bi_{1-x}Sb_x$, Bi_2Te_3, Bi_2Se_3,



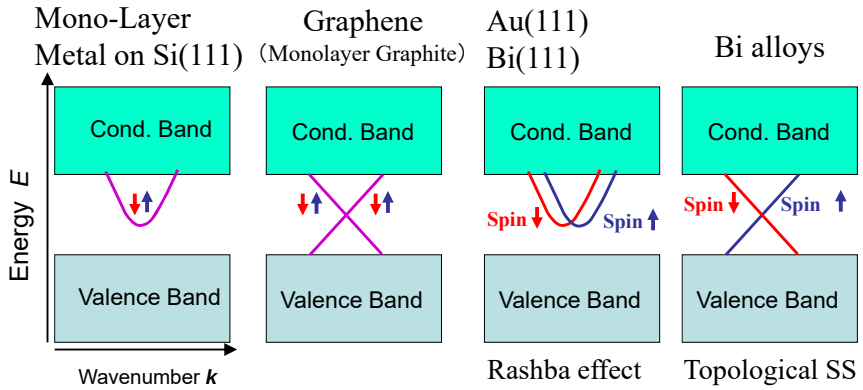


表面空間電荷層

Quantum Hall Effect



Various Surface States



$$E = \frac{p^2}{2m^*} = \frac{\hbar^2 k^2}{2m^*}$$

Free-Electron-like
(Non-relativistic)

$$E = \sqrt{(mc^2)^2 + (pc)^2}$$

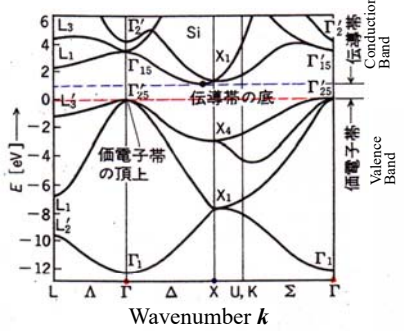
$$m = 0 \quad \text{(Relativistic)}$$

$$E = \pm pc = \pm c\hbar k$$

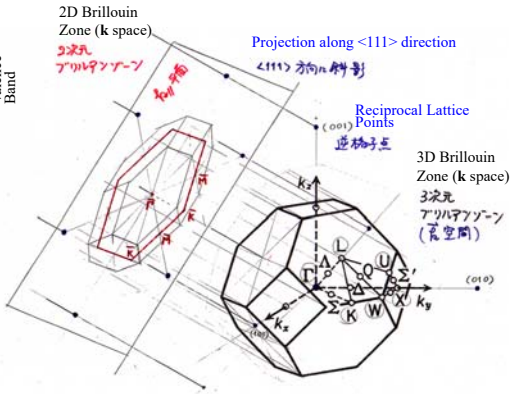
Massless Dirac Electrons

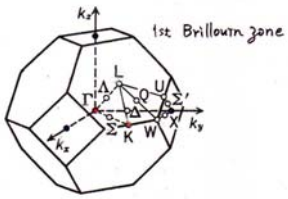
バンド構造とブリルアン領域 Band Structure and Brillouin Zone

3次元 Si 結晶のバンド構造
Bands of Three-Dim. Si Crystal



3次元ブリルアン領域と表面ブリルアン領域





Nearly Free Electron Approximation

拡張ゾーン形式
Extended Zone Scheme

還元ゾーン形式
Reduced Zone Scheme

周期的ゾーン形式
Periodic Zone Scheme

状態密度
Density of States

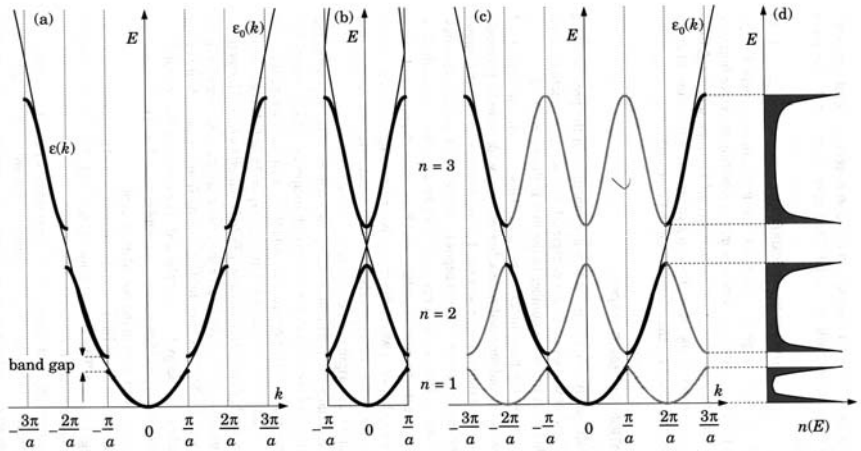
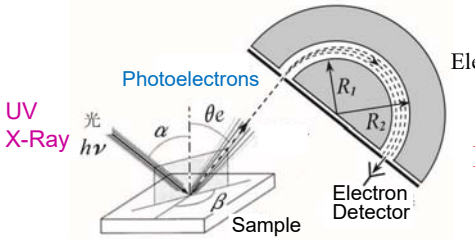


Figure 2.2. Band structure of a one-dimensional crystal in the (a) extended, (b) reduced, and (c) repeated zone schemes, and (d) the density of states as a function of energy. The thick lines show $\varepsilon(k)$ in a weak periodic potential, with bands labelled by n, while the thin parabola is $\varepsilon_0(k)$ for free electrons. The grey lines are periodic repeats.

ARPES (Angle-Resolved Photoemission Spectroscopy)



Electron energy analyzer

Band dispersion $E_b(k_{//})$

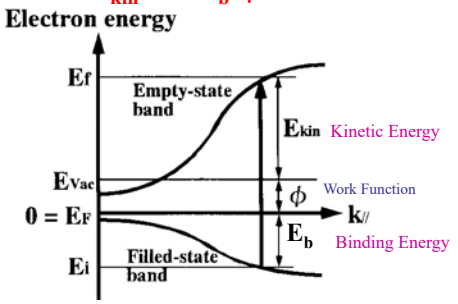
Energy E_b vs. Wavenumber $k_{//}$

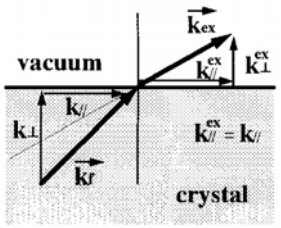
Energy Conservation

$$E_{kin}=h\nu-E_b-\varphi$$

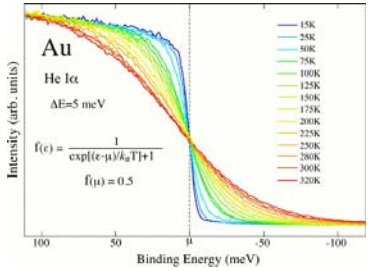
Momentum (Wavenumber) Conservation

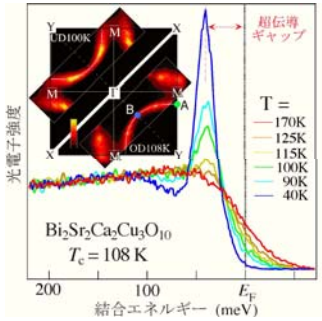
$$k_{//}^{ex}=k_{//}$$

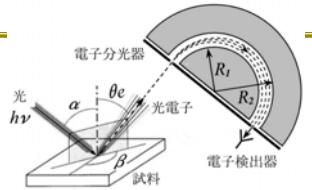




ARPES Apparatus & Spectra



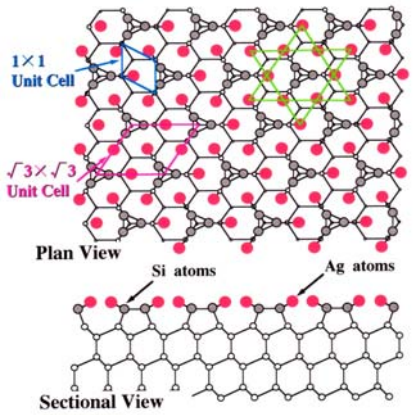


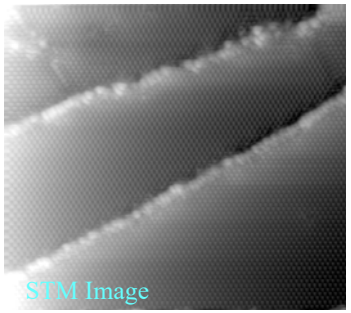


東北大学・理・物理
高橋隆研究室

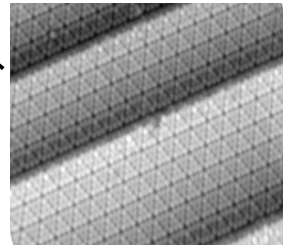
Mono-Layer Ag on Silicon : Si (111)-√3 × √3-Ag Surface

2D Metal





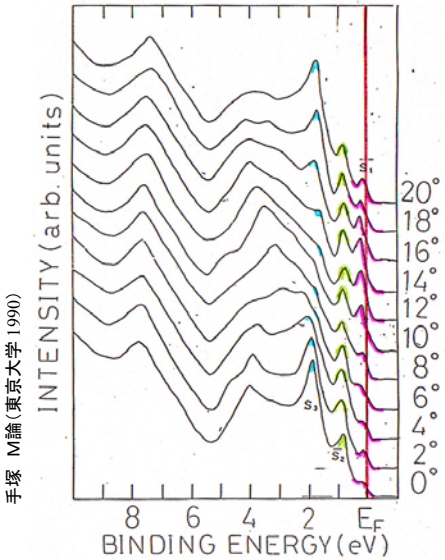
By depositing Mono-layer Ag



Clean Si Surface

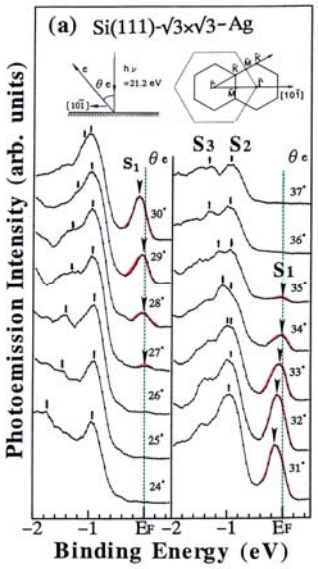
Spectra from Si(111) Surfaces

Si(111)-7×7 Clean Surf.



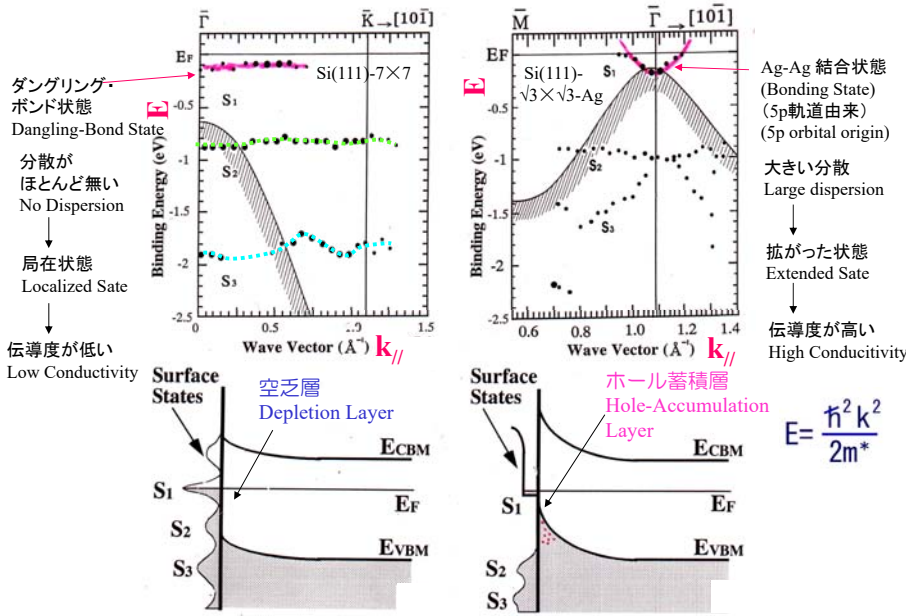
手塚 M論(東京大学 1990)

Si(111)-√3×√3-Ag Surf.



X. Tong, *et al.*, Phys. Rev. **B57**, 9015 (1998)

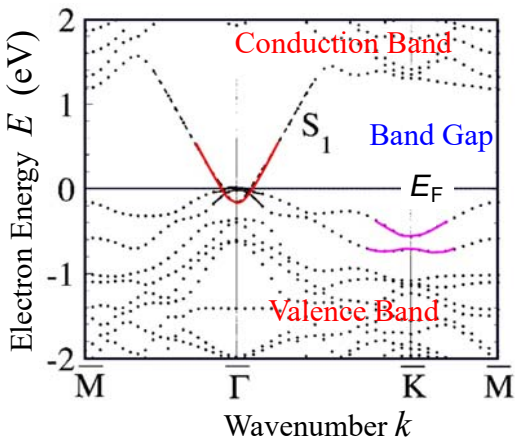
Surface-State Bands & Surface Space-Charge Layer



$$E = \frac{\hbar^2 k^2}{2m^*}$$

Theory: Surface Bands of Monolayer Ag on Si(111)

Surface states are in the bulk band gap.



$$E = \frac{p^2}{2m^*} = \frac{\hbar^2 k^2}{2m^*}$$

Free-electron-like state

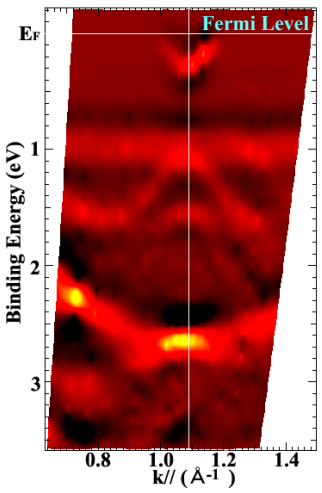
H. Aizawa and M. Tsukada, Surf. Sci. **429** (1999) L509

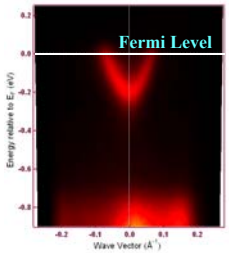
Experiment: Surface Bands of Monolayer Ag on Si(111)

Angle-Resolved Photoemission

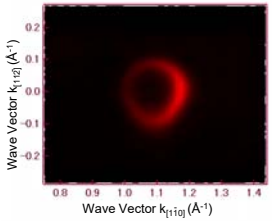
S. Hasegawa, *et al*., Prog. Surf. Sci. **60** (1999) 89.
T. Hirahara, *et al*., e-J. Surf. Sci. Nanotech. **2** (2004) 141.
T. Hirahara, *et al*., Surf. Sci. **563** (2004) 191.

Band Dispersion



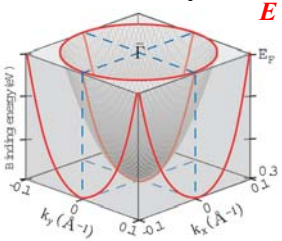


Fermi-Surface Mapping



Parabolic dispersion

m*=0.13m$_e$



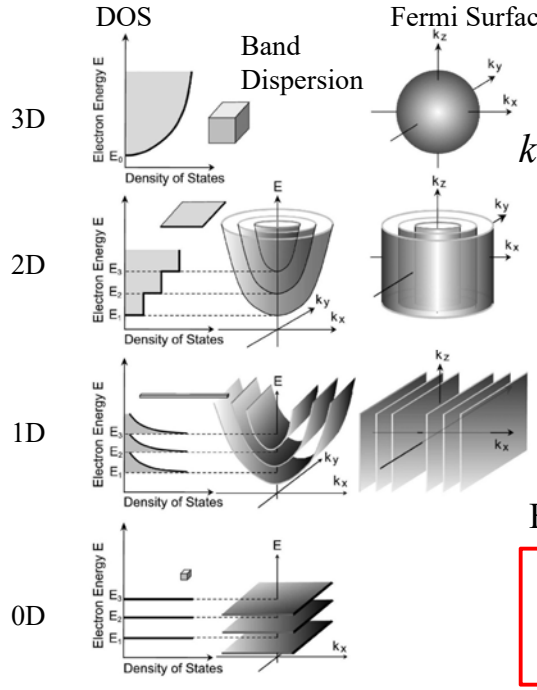
$$E = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*}$$

→ **Free-electron like Metallic state**

Circular Fermi Surface

↓

Isotropic and free-electron-like Metallic 2D electron system



$$k^2 = k_x^2 + k_y^2 + k_z^2$$

$$k^2 = k_x^2 + k_y^2$$

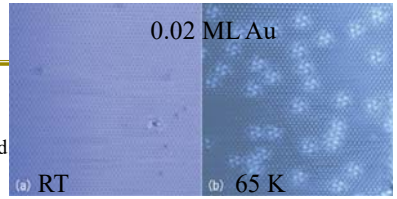
$$k^2 = k_x^2$$

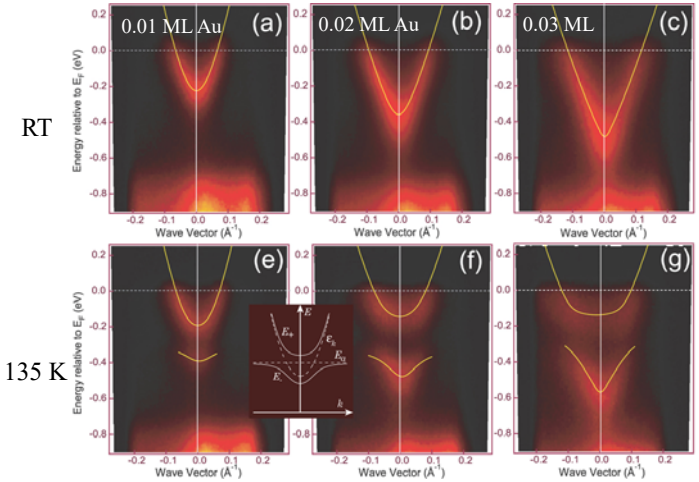
Free-Electron System

$$E = \frac{p^2}{2m^*} = \frac{\hbar^2 k^2}{2m^*}$$

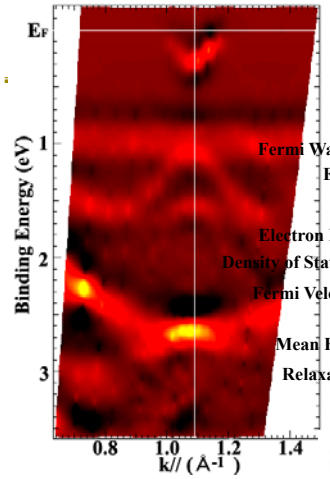
Au Adsorption on Si(111)-√3×√3-Ag

1. Carrier doping in the surface-state band
   ⇒ Increase in band occupation
2. Hybridization of the localized state and surface-state band
   ⇒ Band splitting





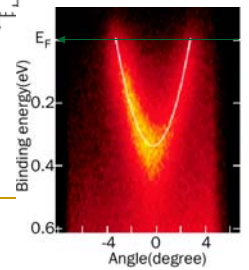
C. Liu, I. Matsuda, R. Hobara, and S. Hasegawa, Phys. Rev. Lett. **96**, 036803 (2006).

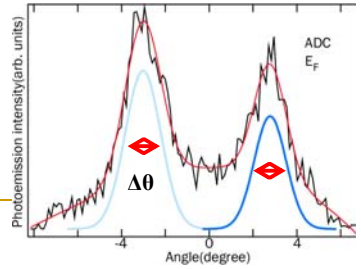


Parameters of Si(111)-√3×√3-Ag Surface

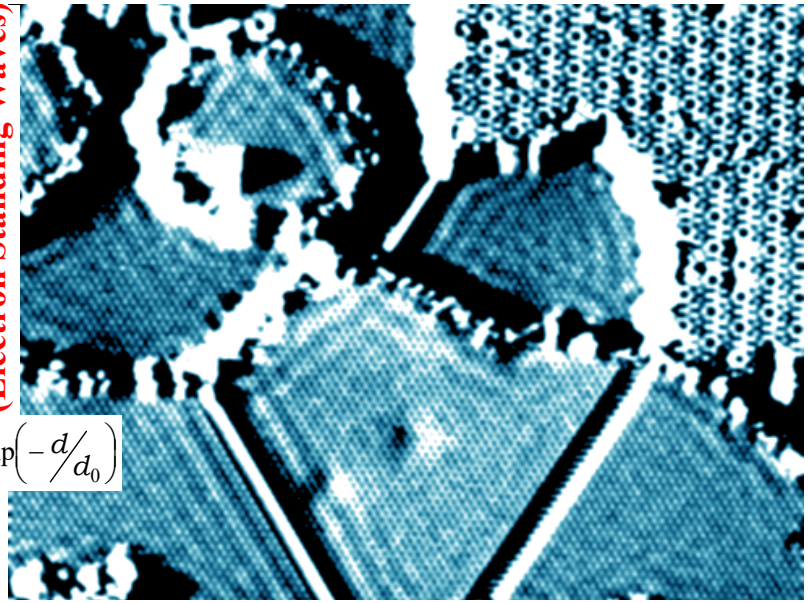
		√3-Ag	√21-Ag
Fermi Wavenumberフェルミ波数	$k_F(\text{Å}^{-1})$	0.10	0.26
Effective Mass有効質量	m^*/m_e	0.13	0.25
	$\Delta\theta$ at $E_F(^\circ)$	~1.7	~1.0
Electron Density 電子濃度	$n = \frac{k_F^2}{2\pi}(10^{14}\text{cm}^{-2})$	0.16	1.1
Density of States状態密度	$\mathcal{D}^{2D} = \frac{m^*}{\pi\hbar^2}(10^{13}\text{eV}^{-1}\text{cm}^{-2})$	5.4	10
Fermi Velocity フェルミ速度	$v_F = \frac{\hbar k_F}{m^*}(10^8\text{cm/s})$	0.89	1.2
	Δk at $E_F(\text{Å}^{-1})$	~0.061	~0.036
Mean Free Path平均自由行程	$l = \frac{1}{\Delta k}(\text{Å})$	~17	~28
Relaxation Time 緩和時間	$\tau = \frac{l}{v_F}(10^{-15}\text{s})$	~1.9	~2.4

Momentum (Angular) Distribution Curve at E_F





電子の海のさざ波
Ripples in electronic sea
(Electron Standing Waves)



$$I_t \propto \rho \cdot \exp\left(-\frac{d}{d_0}\right)$$

$$\rho = |\Psi|^2$$

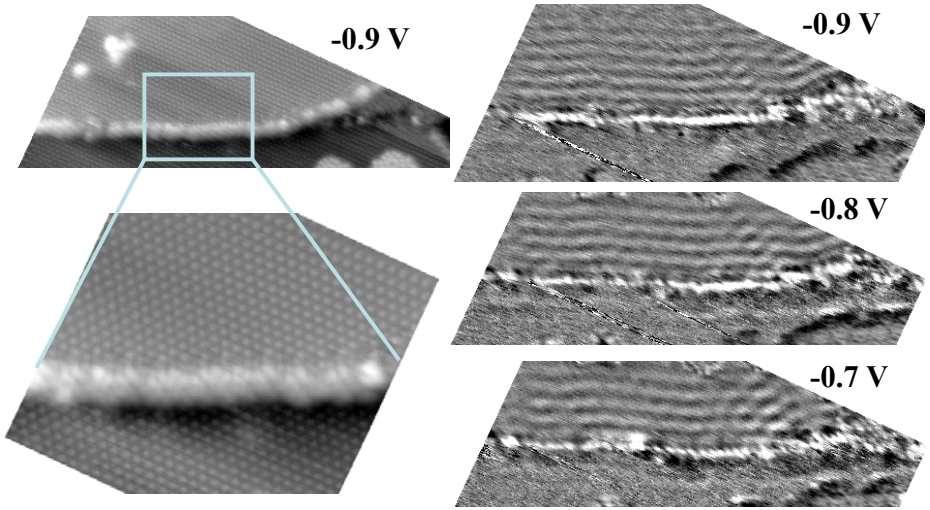
電子の波動関数（の絶対値の２乗）が直接見える!!!

Electron wavefunction (its square of the absolute value) is directly observed!!!

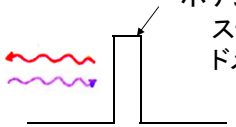
Electron Standing Wave on Si(111)-Ag at 65K

T. Hirahara, et al., Surface Science **563** (2004) 191–198

STM Image | ***dI/dV* Images**



電子定在波 Electron Standing Wave



ポテンシャル障壁 Potential Barrier
ステップ Step
ドメイン境界 Domain Boundary

$\rho(E, x)$（局所状態密度 Local DOS）

$\propto |\Psi_i+\Psi_r|^2$

$\propto \{1+|R|^2+2|R|\cos(2k_x \cdot x-\eta)\} \cdot |u(x,y)|^2$

定在波 Standing Wave　　原子像 Atomic Arrangement

2次元　ブロッホ波 2D Bloch Wave

入射波 $\Psi i=\exp[i(k_x \cdot x+k_y \cdot y)] \cdot u(x, y)$

Incident Wave $E=E_0+\frac{\hbar^2}{2m^*}(k_x^2+k_y^2)$

$u(x,y)$= cell function

定在波の波長 $\lambda=\frac{\pi}{k_x}$

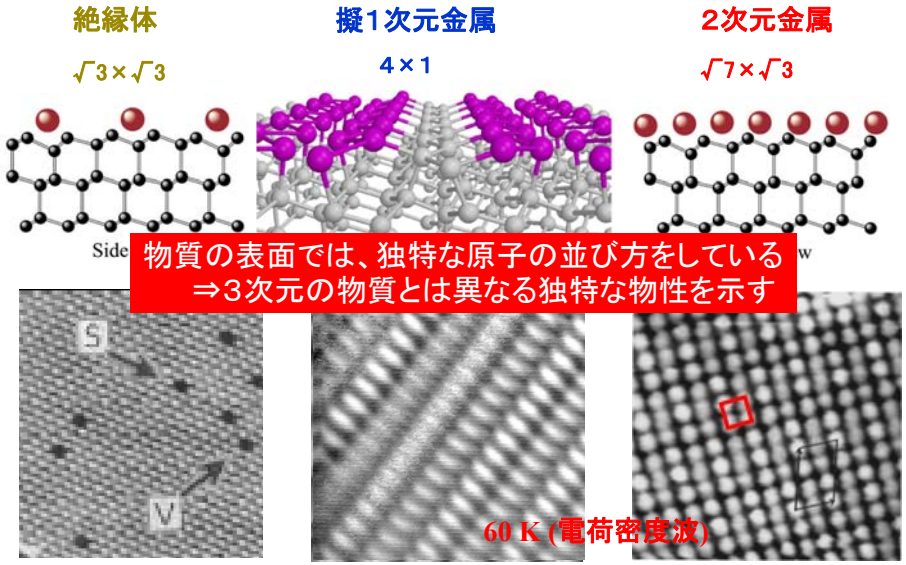
Wavelength of Standing Wave

反射波　$\Psi_r=R \cdot \exp[i(-k_x \cdot x+k_y \cdot y)] \cdot u(x, y)$

Reflected Wave　$R=|R| \cdot \exp[i\eta]$

η: 反射位相シフト Reflection Phase Shift

インジウム吸着Si(111) 表面



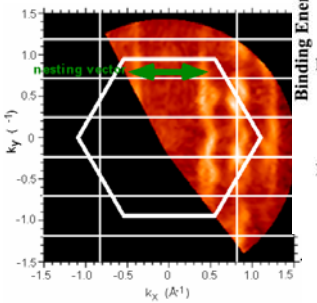
A. A. Sarranin, et. al.　　H. Y. Yeom, et al., PRL **82**, 4898 (1999)　　S. L. Surnev, et. al.

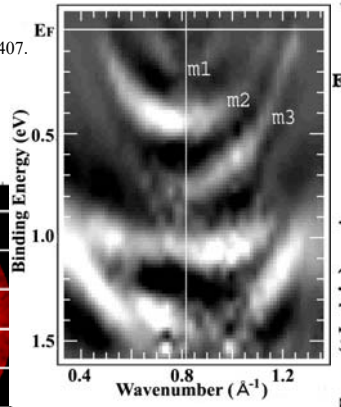
Surface-State Bands of Si(111)-4×1-In Surface

-Quasi-1D Metallic Surface → Anisotropy in Conductivity
-Peierls Instability
Charge-Density Wave (CDW) → Metal-Insulator Transition
→ Temperature Dependence of Conductivity

H. Morikawa, et al.
表面科学 **25** (2004) 407.

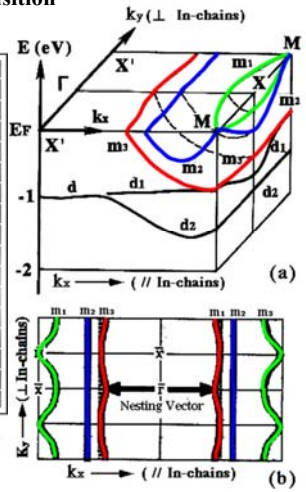
H.-W. Yeom, et al.
PRL **82** (1999) 4898





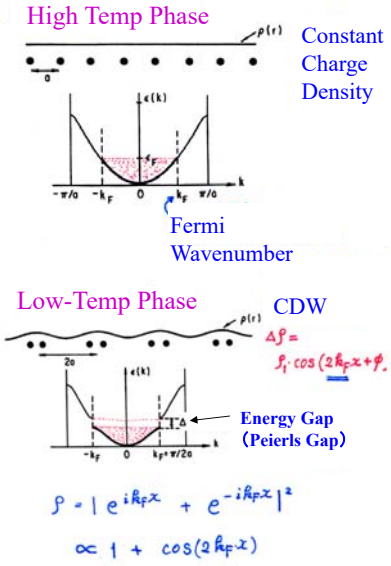
Linear Fermi Surfaces
Bisecting the Brillouin Zone

Band Dispersion
T. Abukawa, S. Kono, et al.
Surf. Sci. **325** (1995) 33

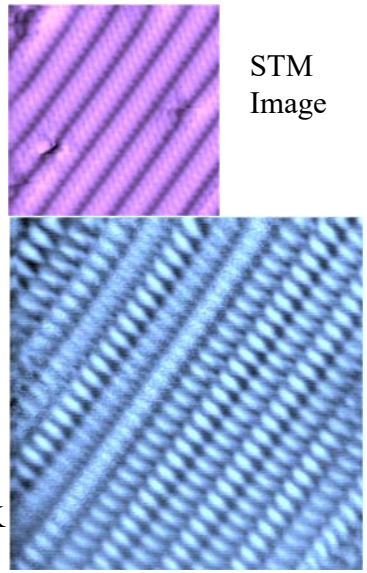


Fermi Surface Mapping

Peierls Transition —(Quasi-) 1D Metal



Si(111)-4×1-In Surface

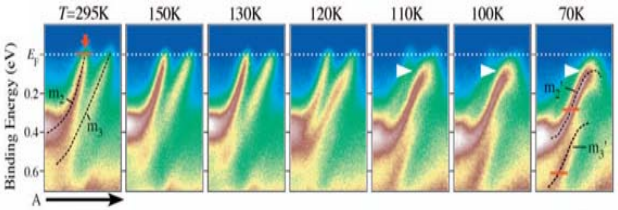


STM
Image

RT

70K

Metal-Insulator Transition at Si(111)-4×1-In Surface

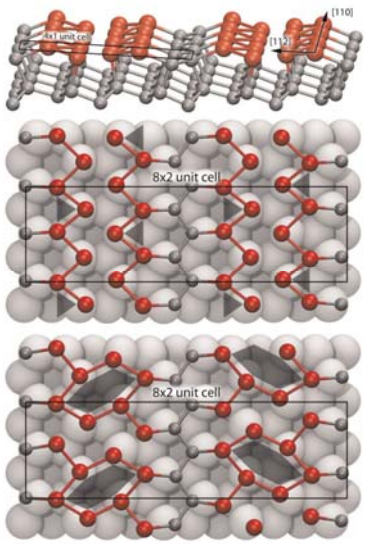


Y.J.Sun *et al.*, PRB **77**, 124115 (2008)

MI Transition at～110 K
With CDW
⇒ Peierls Transition

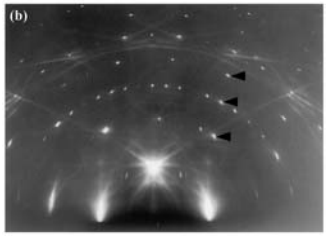
H.W.Yeom *et al.*, PRL **82**, 4898 (1999)

Atom Displacements (Lattice Distortion) with CDW

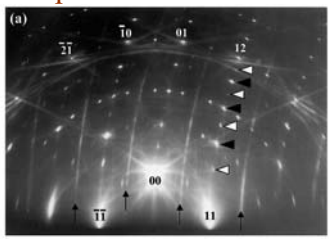


W. G. Schmidt, et al.,
Phys. Status Solidi B 249, No. 2, 343–359 (2012)

反射高速電子回折（RHEED）



High-Temp Phase RT

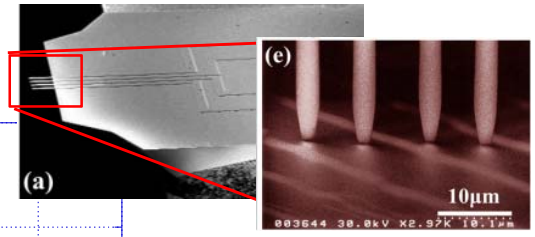


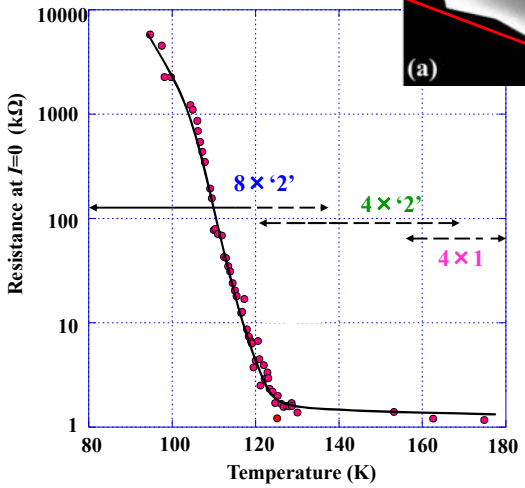
100 K

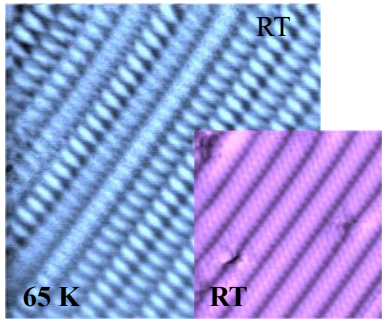
Low Temp Phase

Electrical Resistance of Si(111)-4×1-In Surface

T. Tanikawa, *et al.*,
Phys. Rev. Lett. **93** (2004) 016801.



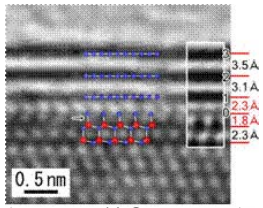




CDW Phase (8×'2') Metal Phase (4×1)

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

Graphene on SiC crystal surface



(M. Kusunoki @ Nagoya U.)

Relativistic（Dirac electron

$$E = \sqrt{(mc^2)^2 + (pc)^2}$$

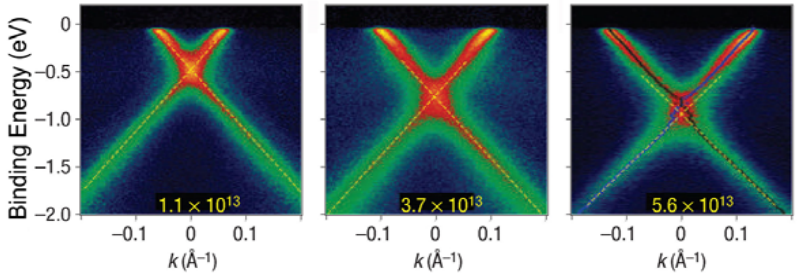
$m = 0$ Zero Mass

High mobility

$$E = \pm\hbar ck$$

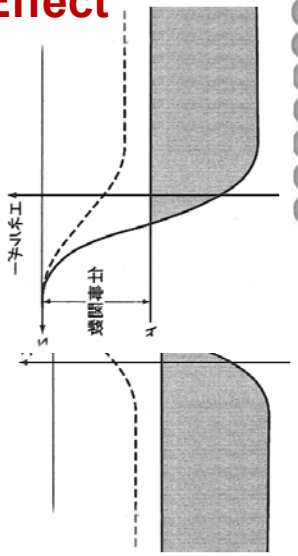
Non-relativistic

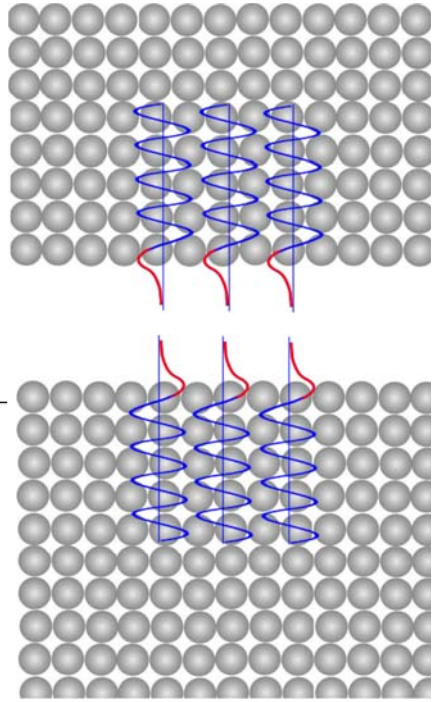
$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$



A. Bostwick, et al., Nature Physics **3**, 36 (2007).

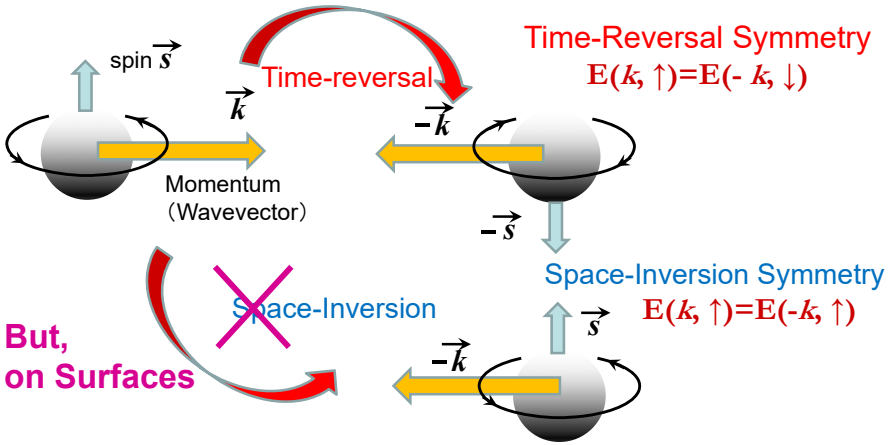
Rashba Effect





Emmanuel I. Rashba

The electron energy is determined by its momentum (and spin).



Time-Rev. Sym.＋Space-Inv. Sym.⇒ Spin(Kramers) Degenera

Spin-Split in Surface States ⇐ $E(k,\uparrow)\neq E(k,\downarrow)$

Difference in Energy between Spin↑ and Spin↓

$$H=\frac{1}{2m}p^2+V(x)+\boxed{\frac{1}{4mc^2}\sigma\cdot\left(\mathrm{grad}\,V\times p\right)}$$

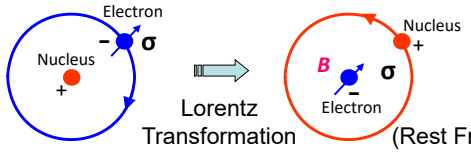
Spin-Orbit-Coupling Hamiltonian

$\left(\mathrm{grad}\,V\times p\right)$ = Effective Magnetic Field ***B***

Orbital Motion of Electron ⇒ Orbital Motion of Nucleus ⇒ Eff. Mag. Field ***B***

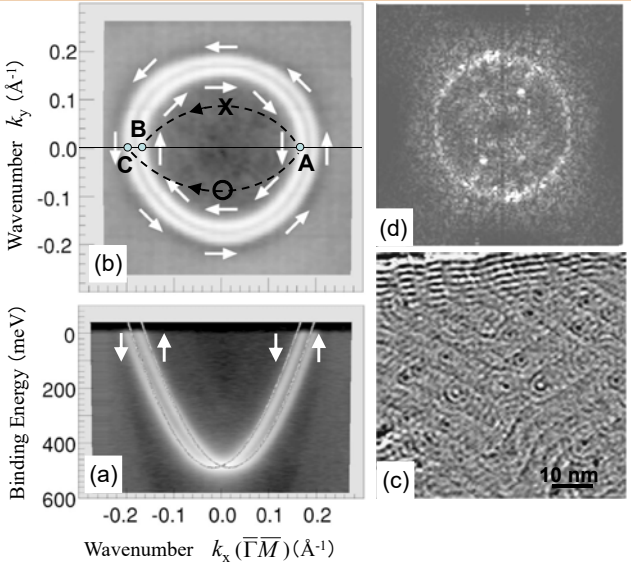
⇓

Interact with spin σ



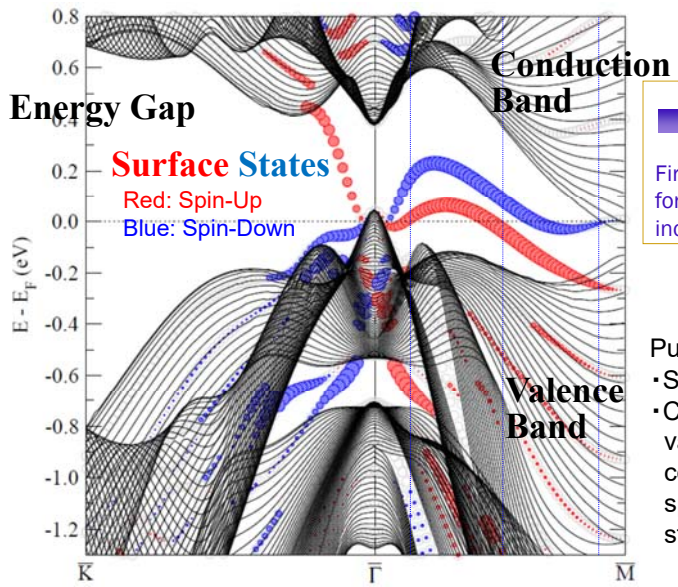
Difference between ↑ and ↓
=Zeeman Energy by Eff. Mag. Field *B*

Surface States of Au(111)—Spin split due to Rashba effect—



(a) (b) G. Nicolay, et al., Phys. Rev. B **65**, 033407 (2001).
(c)(d) L. Petersen, et al., Phys. Rev. B **58**, 7361 (1998).

Band Dispersion of 20 Atomic Layer Bi(111) slab
(1st Principles Calculation)



Bihlmayer
(Juhlich, Germany)

vacuum
Bi
vacuum
First-principles calculation for free-standing Bi slabs including SOC

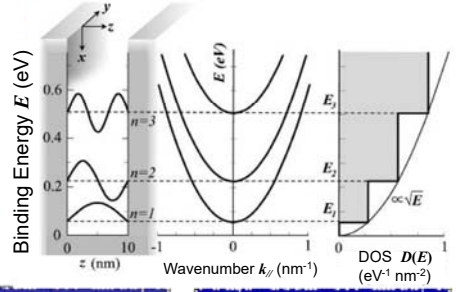
Pure Bi
- Semi-metal in Bulk
- Conduction band and valence band are connected by the spin-split surface states

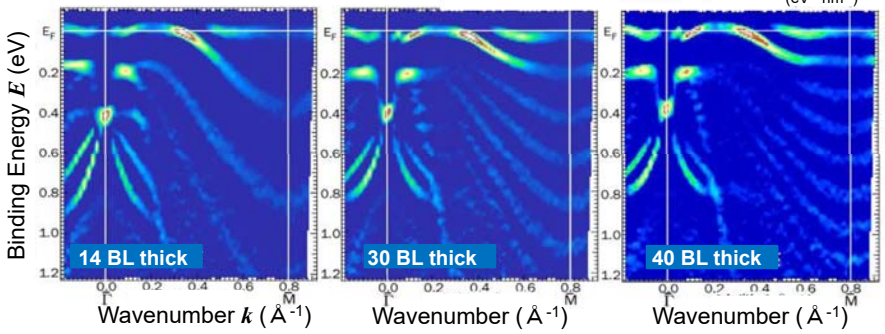
ARPES of Bi(111) Ultrathin films —QWS and SS—

T. Hirahara, et al.,
Phys. Rev. Lett. **97**, 146803 (2006).

Quantum-Well States
Surface States

Conductivity of Bi thin film
= surface-state conductivity

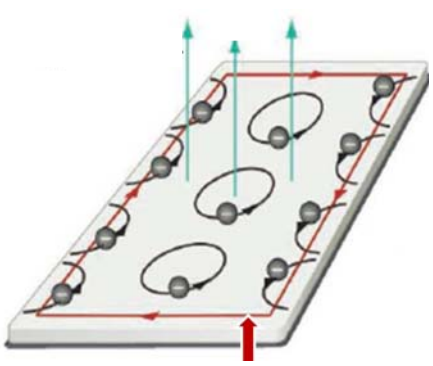


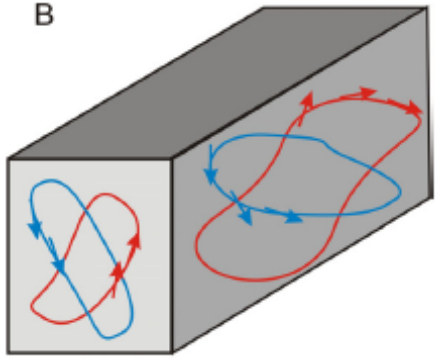


Topological Surface States

$Bi_{1-x}Sb_x$, Bi_2Te_3, Bi_2Se_3,

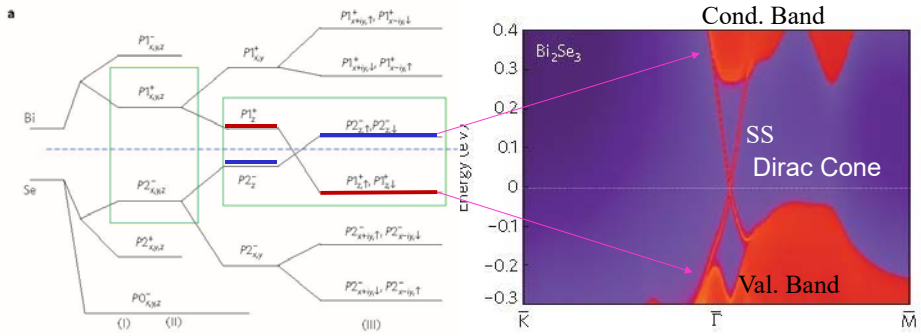
Analogue of Edge States in Quantum Hall States (2DEG)
⇒ Extension to 3D Materials
⇐ Strong SO Interaction produces effective B.





Electronic States of Bi_2Se_3 (Theory)

H. Zhang, et al., Nature Physics (May 2009)

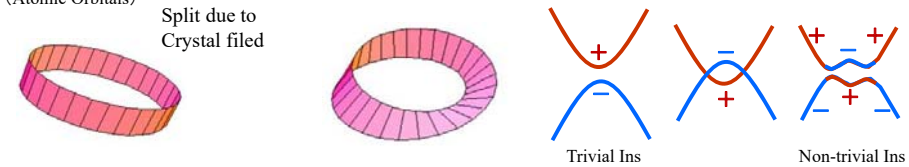


Isolated Atom
(Atomic Orbitals)

Atomic Bondings

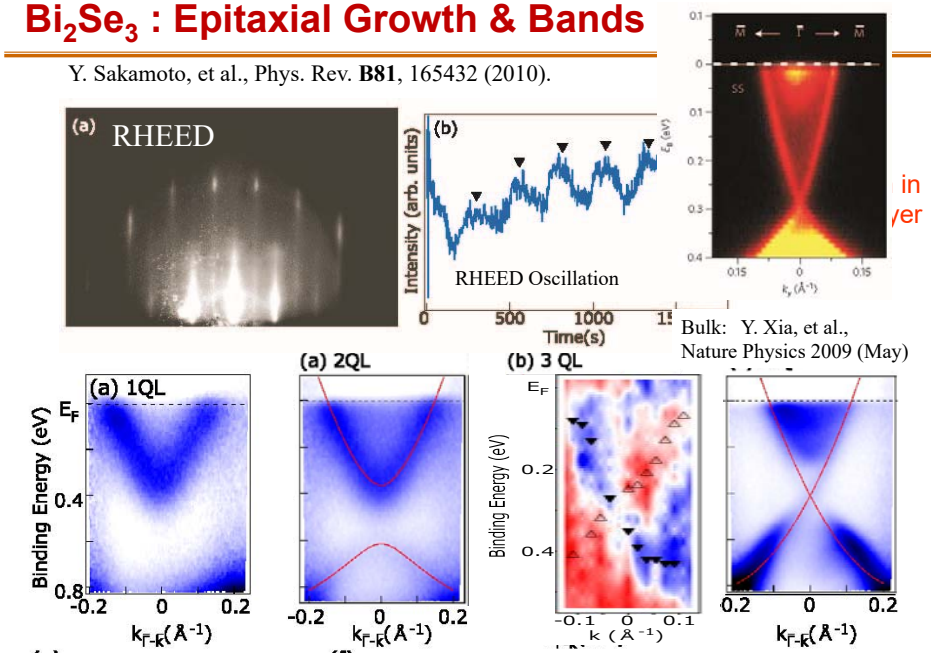
Split due to
Crystal filed

Spin-Orbit Intercation

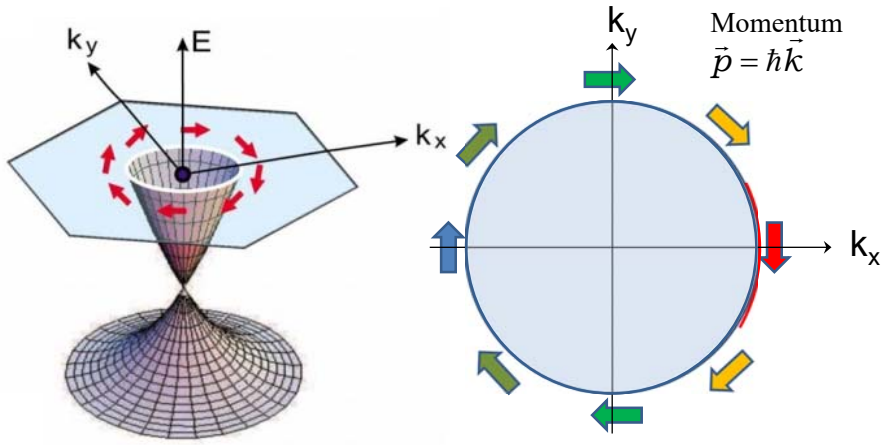


Bi_2Se_3 : Epitaxial Growth & Bands

Y. Sakamoto, et al., Phys. Rev. **B81**, 165432 (2010).



Chiral Dirac Cone of Topological Insulators and Current-Induced Spin Polarization

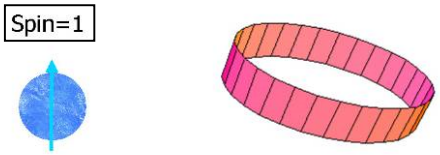


M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010)

Chiral Fermi Surface

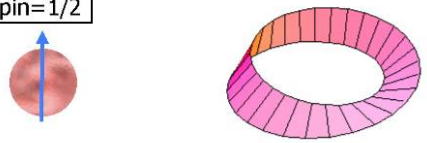
2π-rotation of spin

Spin=1



$\Psi \xrightarrow[\text{2π-rotation}]{} \Psi$

Spin=1/2

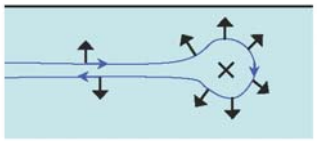


$\Psi \xrightarrow[\text{2π-rotation}]{} -\Psi$

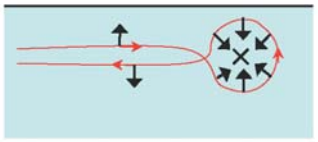
Spinor

Time-Reversal Symmetry

$E(k,\uparrow)=E(-k,\downarrow)$



$\Psi_{initial} \xrightarrow[\text{π-rotation}]{} \Psi_{scattered1}$



$\Psi_{initial} \xrightarrow[\text{-π-rotation}]{} \Psi_{scatter2}$

$\Psi_{scatter2} = -\Psi_{scatter1}$

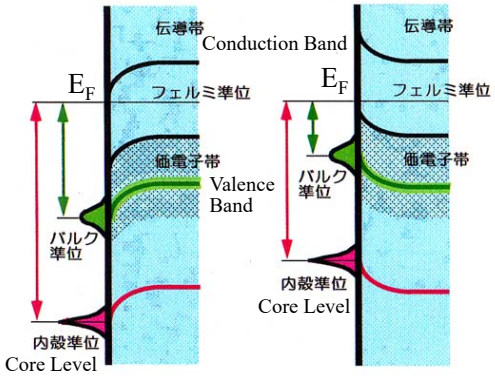
$\Psi_{scatter1} + \Psi_{scatter2} = 0$

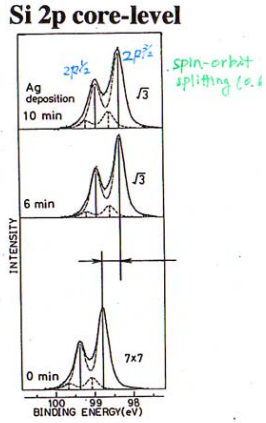
Destructive interference ⇒ **No backscattering**

⇒ **High mobility**

Band Bending of Bulk States Near Surface

Energy difference between E_F and a core level Measured by Photoemission Spectroscopy

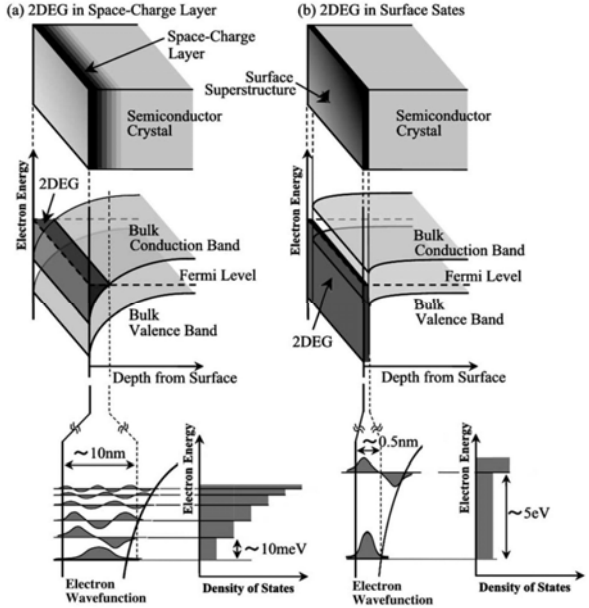




Si $(1s)^2(2s)^2(2p)^6$ $(3s)^2(3p)^2$
core level valence band

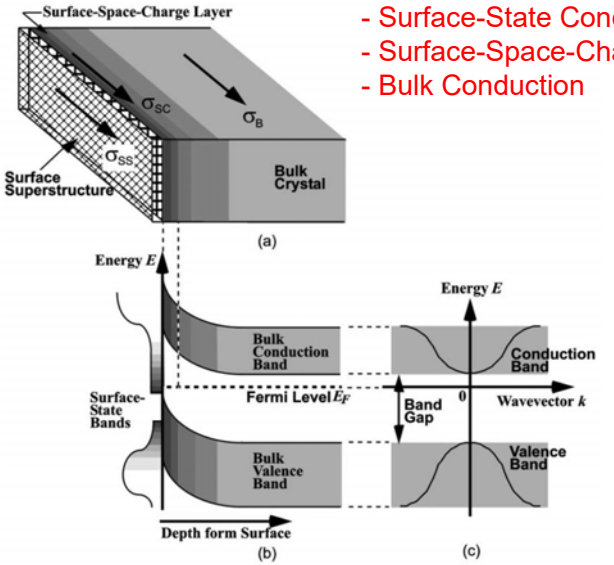
Si(111)-√3x√3-Ag
Fermi level shift ; 0.5 eV
S. Kono, et al.
Phys. Rev. Lett. 58 (1993) 113

Surface States & Surface-Space-Charge Layer（Band bending）



S. Hasegawa & F. Grey
Surface Science
500 (2002) 84–104

Three Channels for Electrical Conduction near Surface



- Surface-State Conduction
- Surface-Space-Charge-Layer Conduction
- Bulk Conduction

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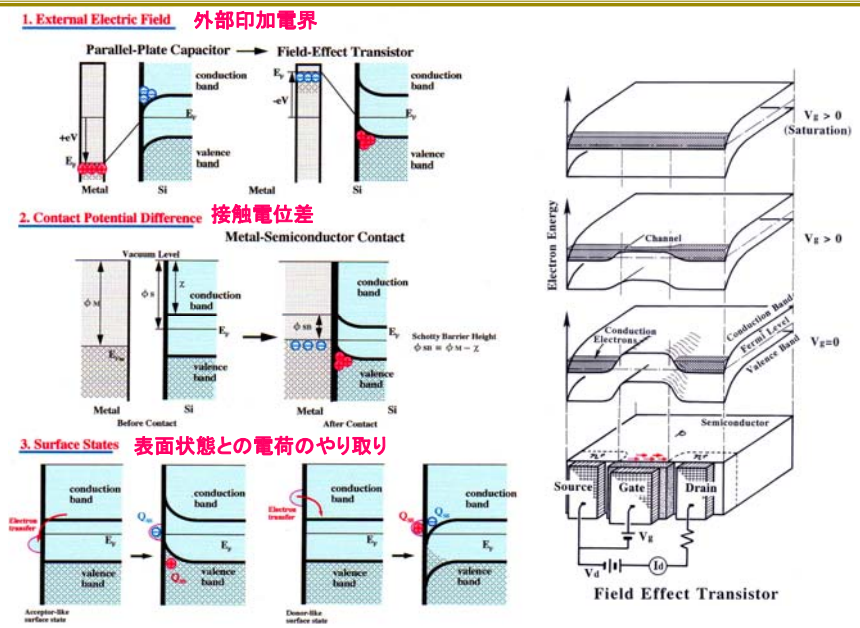
Origins of Band Bending (Origins of SSCL)