Studies on surface systems by using electron spectroscopy with synchrotron radiation and positron diffraction

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Physical properties at a surface

Surface atomic structure	Surface electronic structure
Diffraction	**Spectroscopy**
陽電子回折 Positron Diffraction	光電子分光 Photoemission spectroscopy

- Mystery of the 2-D ordered metal alloy on a surface
- Introduction of our time-resolved photoemission station at synchrotron radiation facility

合金（Metal Alloy）

Hume-Rothery phase

Chapter 21, C. Kittel,
"*Introduction to Solid State Physics*",
(1996)

electron/atom ratio of electron compounds

Alloys	fcc	bcc	γ	hcp
Cu-Zn	1.38	1.48	1.58-1.66	1.78-1.87
Cu-Al	1.41	1.48	1.63-1.77	
Cu-Si	1.42	1.49		
Ag-Cd	1.42	1.50	1.59-1.63	1.65-1.82

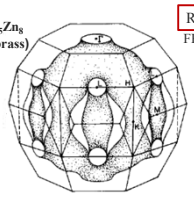
A close relation between the Fermi surface and the Brillouin zone
(*electron/atom*) (the crystal structure)

Two competing theoretical model

Jones theory vs Pseudopotential approach (Pair potential interpretation)

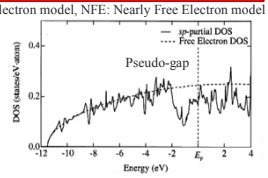
- **Jones theory for alloying**

Cu_5Zn_8 (γ-brass)



Reduction of electrons at the highest kinetic energy

FE: Free Electron model, NFE: Nearly Free Electron model



合金（Metal Alloy）

- **Pair potential interpretation**

(long-range interaction mediated by conduction electrons)

w: individual ion pseudopotential

$$E(k)=\frac{\hbar^2k^2}{2m}+<k|w|k>+\sum_q\frac{S^*(q)S(q)<k|w|k+q><k+q|w|k>}{\hbar^2/2m[k^2-(k+q)^2]}$$

Band structure energy E_{bs} =ΣS(q)*S(q)F(q)

Fourier Transform

$$E_{bs}=\frac{1}{2N}\sum_{i\neq j}V_{pair}(r_i-r_j)+\frac{1}{N}\sum_q F(q)$$

Ion-pair potential(structure dependent)

$$V_{pair}(r_i-r_j)=\frac{2}{N}\sum_{i\neq j}F(q)\exp(-iq\cdot(r_i-r_j))$$

$$V_{3D}\propto\frac{\sin(2k_Fd+2\delta_F)}{(k_Fd)^3}$$

Ion pair-interaction via the 3-D Friedel oscillation

Motivation

合金（Metal Alloy）

Formation of metal alloys
of the electron compounds

Fermi wavenumber, Fermi surface

Crystal structure

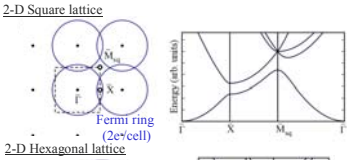
表面合金（Surface Metal Alloy）

Any metallic surface superstructure with electron compound nature?

In-plane Fermi wavenumber, 2-DFermi surface

Surface ordered phase

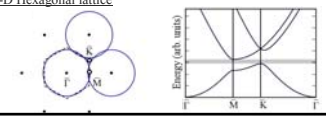
2-D Square lattice



Fermi ring (2e⁻/cell)

2e⁻/cell
=> Metallic

2-D Hexagonal lattice

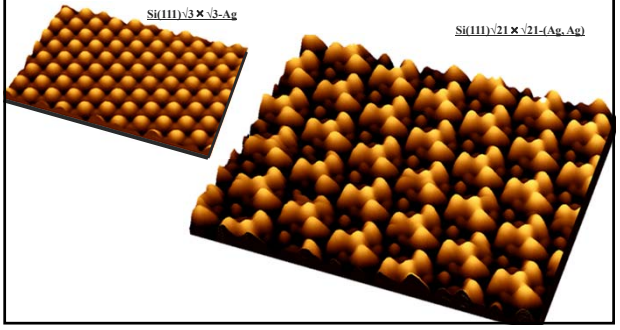


2e⁻/cell
⇒ Insulating
⇒ Complete gap-opening
⇒ Not pseudo-gap!!

Surface Metal Alloy (2-D Metal Alloy) on Semiconductor Substrate

Ag | Cu | Ag | Au | Na | K | Cs

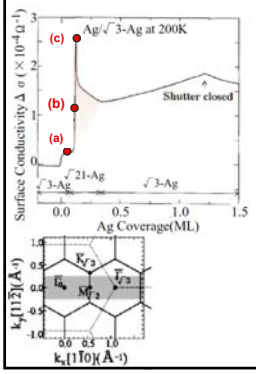
Si(111)7×7 —(Ag: 1ML, 470~870K)→ Si(111)√3×√3-Ag —(Ad: 0.1~ 0.2ML, < 200~300 K)→ Si(111)√21×√21-(Ag, Ad)



Electron doping

I. Matsuda, T. Hirahara *et al.*, Phys. Rev. **B 71**, 235315 (2005)

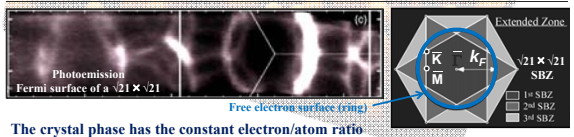
Fermi surface



Surface Metal Alloy (2-D Metal Alloy) on Semiconductor Substrate

The √21 × √21 phase on Si(111)

Initial surface phase (coverage)	adatom (coverage)	formation temperature	total coverage	a number of valence electrons	
2-D surface phase					
√3 × √3-Ag (1.0 ML)	Au (0.1~0.2ML)	LT	1.1~1.2 ML	3/unit cell [1]	
√3 × √3-Ag (1.0 ML)	Ag (0.1~0.2ML)	LT	1.1~1.2	3	[2]
√3 × √3-Ag (1.0 ML)	Na (0.1~0.2ML)	LT	1.1~1.2	3	[2]
√3 × √3-Ag (1.0 ML)	K (0.1~0.2 ML)	LT	1.1~1.2	3	[3]
√3 × √3-Ag (1.0 ML)	Cs (0.1~0.2 ML)	LT	1.1~1.2	3	[3]
√3 × √3-Au (~0.9 ML)	Ag (0.2~0.3 ML)	HT	1.1~1.2	3	[4]
1-D surface phase					
5x2-Au (0.4~0.5 ML)	Ag (~0.7 ML)	HT	1.1~1.2	3	[5]
3x1-Ag (0.3ML)	Au(0.8ML)	HT	1.1~1.2	3	[6]



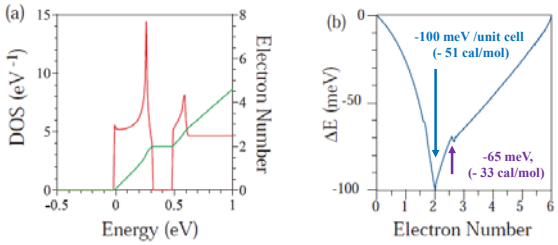
The crystal phase has the constant electron/atom ratio → electron compound nature

[1] J. N. Crain *et al.*, Phys. Rev. B **66**, 205302(2002). [2] I. Matsuda *et al.*, Phys. Rev. B **71**, 235315 (2005). [3] H. M. Zhang *et al.*, Phys. Rev. **B 70**, 245301 (2004). [4] Y. Yuhara *et al.*, Surf. Sci. **326**, 133 (1995). [5] I. Matsuda *et al.*, Phys. Rev B **82**, 165330 (2010). [6] F. Nakamura *et al.*, submitted.

Jones theory for surface (2-D) alloying

$$\text{Energy difference} = \int_0^{E_{F1}} E\cdot DOS^{NFE}(E)dE - \int_0^{E_{F2}} E\cdot DOS^{FE}(E)dE$$

NFE Energy　　FE Energy



the order of 100 cal/mol for noble metal alloys

Prog. Mat. Sci. **22**, 151 (1978).

Energy stabilization but the minimum at two electrons (insulating)

Pair potential interpretation

Ion pair-interaction via the 2-D Friedel oscillation

band structure energy: $\Delta E = \sum_{ionpairs} -\varepsilon_F \left(\frac{2\sin(\delta_F)}{\pi}\right)^2 \frac{\sin(2k_F d - 2\delta_F)}{(k_F d)^2}$

k_F

n=1 : k_F=0.153[Å^{-1}]
n=2 : k_F=0.216[Å^{-1}]
n=3 : k_F=0.265[Å^{-1}]
n: electrons/unit cell

Photoemission Fermi surface mapping

d(d')

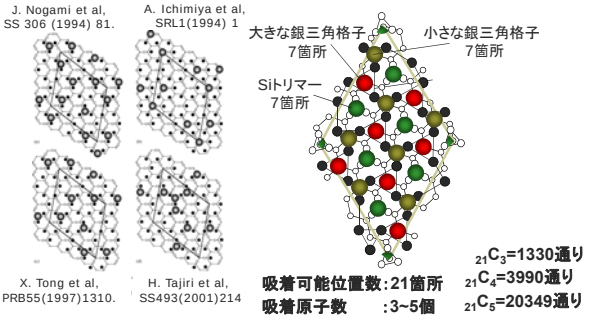
Distance between two adatoms (up to the 11th nearest neighbors)

Structure analysis

Structure analysis of the √21x√21 phase

Si(111)7×7 —Ag: 1ML, 470~870K→ Si(111)√3×√3-Ag —Ag: 0.1~ 0.2ML, LT→ Si(111)√21×√21-(Ag, Ag)

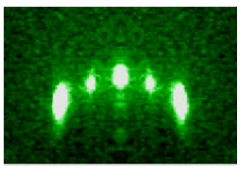
J. Nogami et al, SS 306 (1994) 81.　A. Ichimiya et al, SRL1(1994) 1



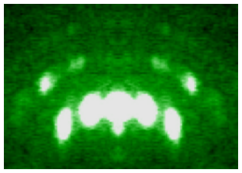
X. Tong et al, PRB55(1997)1310.　H. Tajiri et al, SS493(2001)214

吸着可能位置数:21箇所　$_{21}C_3$=1330通り
吸着原子数　:3~5個　$_{21}C_4$=3990通り　$_{21}C_5$=20349通り

Positron Diffraction

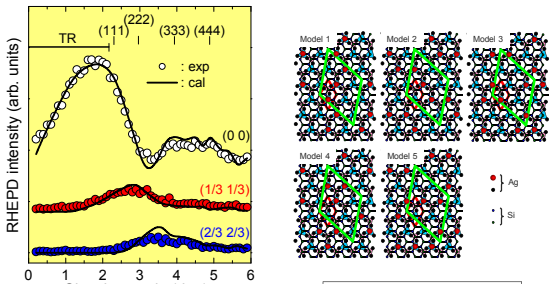


the √3x√3 phase



the √21x√21 phase

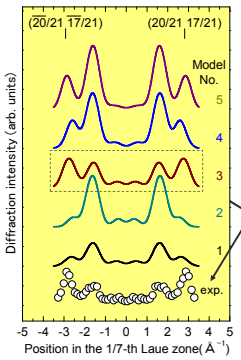
Positron Diffraction

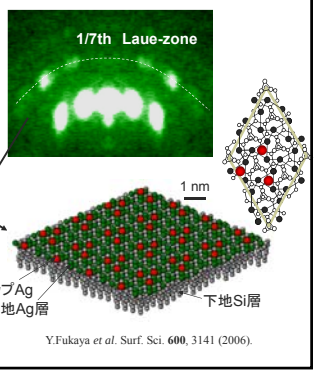


吸着サイト：大きな Ag三角格子
吸着数　：3箇所

5通りが選別されるが
有意差はない

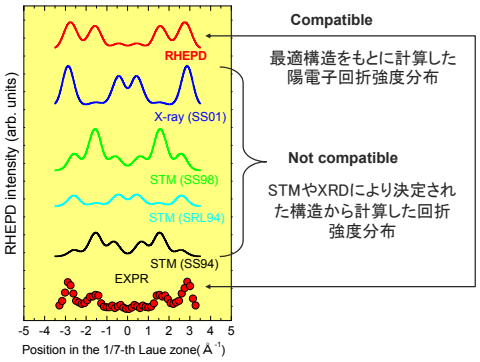
Positron Diffraction





Y.Fukaya *et al.* Surf. Sci. **600**, 3141 (2006).

Positron Diffraction



Compatible

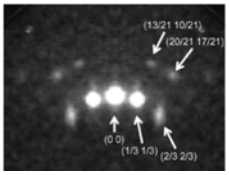
最適構造をもとに計算した陽電子回折強度分布

Not compatible

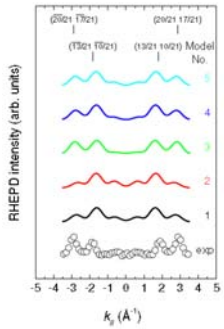
STMやXRDにより決定された構造から計算した回折強度分布

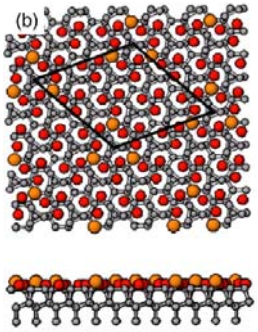
Positron Diffraction

Si(111)7×7 —(Au: 0.4~0.5ML, 790K)→ Si(111)5×2-Au —(Ag: 0.6~ 0.7ML, HT)→ Si(111)√21×√21-(Ag, Au)



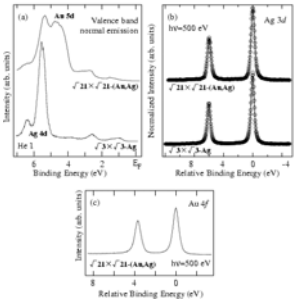
Positron Diffraction

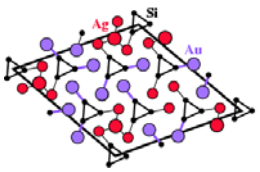




Y.Fukaya *et al.* e-J. Surf. Sci. Nanotech. **7**, 432 (2009).

Core-level photoemission spectra

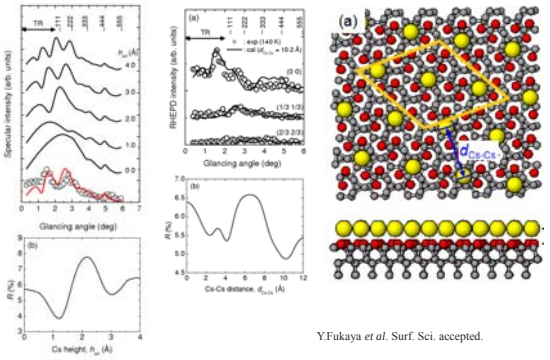




Y.Fukaya *et al.* Surf. Sci. **606**, 919 (2012).

Positron Diffraction

Si(111)7×7 —Ag: 1ML, 470~870K→ Si(111)√3×√3-Ag —Cs: 0.1~0.2ML, LT→ Si(111)√21×√21-(Ag, Cs)

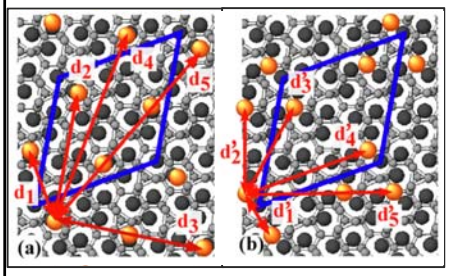


Y.Fukaya *et al*. Surf. Sci. accepted.

Pair potential interpretation

Ion pair-interaction via the 2-D Friedel oscillation

band structure energy: $\Delta E = \sum_{ionpairs} -\varepsilon_F \left(\frac{2\sin(\delta_F)}{\pi}\right)^2 \frac{\sin(2k_F d - 2\delta_F)}{(k_F d)^2}$



Alkali metal adatom　　Noble metal adatom

k_F

n=1 : k_F=0.153[Å^{-1}]
n=2 : k_F=0.216[Å^{-1}]
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n: electrons/unit cell

d(d')

Distance between two adatoms (up to the 11th nearest neighbors)

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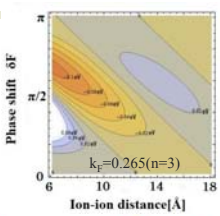
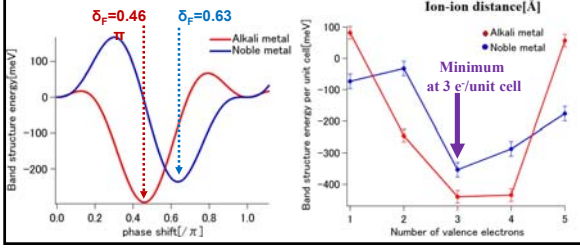




Phase shift analyses

Alkali metal adatom

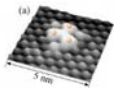
δ_F=0.46π

- Friedel sum rule, s-wave, +1 charge:
  δ_F=0.5π
- Cs/Cu(111),
  Th von Hofe *et al*. Phys. Rev B **73** 245434 (2006).
  δ_F=(0.43±0.08)π

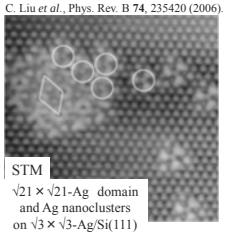
Noble metal adatom

δ_F=0.63π

- Standing wave around a Ag nanocluster
  (a precursor of the √21 × √21-Ag phase)



C. Liu *et al*., Phys. Rev. B **74**, 235420 (2006).



STM
√21 × √21-Ag domain and Ag nanoclusters on √3 × √3-Ag/Si(111)

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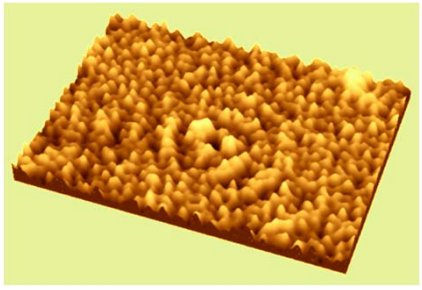
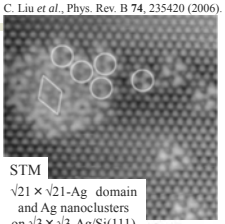


東大物性研　長谷川幸雄研

Phase shift analyses

C. Liu *et al*., Phys. Rev. B **74**, 235420 (2006).



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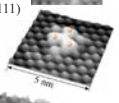
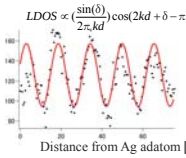
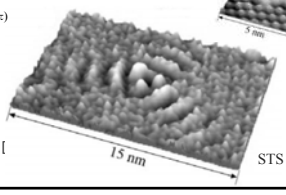


$LDOS \propto \left(\frac{\sin(\delta)}{2\pi kd}\right)\cos(2kd + \delta - \pi)$



Distance from Ag adatom [

δ=(0.61±0.05)π

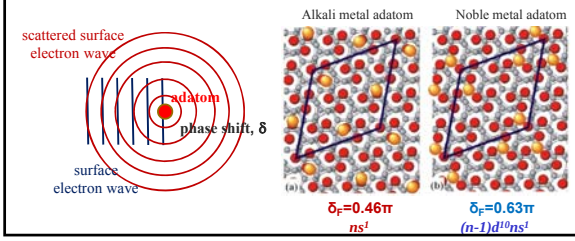


STS

I. Matsuda *et al.*, Phys. Rev. B **82**, 165330 (2010).

- The $\sqrt{21} \times \sqrt{21}$ phases, prepared by **eight** different procedures, show the constant number of total metal coverage and a number of valence electron, showing surface electron compound nature.
- The Anderson's idea and the Jones model do find electron stability by the surface superstructure formation. However, they fails to explain a number of valence electrons and the experimental band feature.
- The pair potential interpretation (the pseudopotential approach) explains all the experimental results, indicating importance of medium-range interatomic interaction, mediated by the 2-D surface-state electrons.

The $\sqrt{21} \times \sqrt{21}$ superstructure model



$\delta_F = 0.46\pi$ ns^1 $\delta_F = 0.63\pi$ $(n-1)d^{10}ns^1$

Acknowledgements

Y. Fukaya, A. Kawasuso, and A. Ichimiya