### Photoemission from a surface scientist's view

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Heinrich Rudolf Hertz



### **Albert Einstein**

# What is Light ? Electromagnetic (EM) waves

 Hertz helped establish the photoelectric effect (which was later explained by Albert Einstein) when he noticed that a charged object loses its charge more readily when illuminated by ultraviolet light. In 1887, he made observations of the photoelectric effect and of the production and reception of electromagnetic (EM) waves.

## Original photoelectric experiment



**Figure 1.** Typical experimental setup for the demonstration of the photoelectric effect as used by Hallwachs [8]. Light from a spark gap, with the option of being screened (Schirm) or filtered (Gips), impinges on a charged gold-leaf electroscope with a grounded body (Erde). A negatively charged electroscope could be discharged by ultraviolet light, whereas positive charge could not be removed.

#### New Journal of Physics 7 (2005) 97

## Photoelectric Effect Apparatus

- When the tube is kept in the dark, the ammeter reads zero
- When plate E is illuminated by light having an appropriate wavelength, a current is detected by the ammeter
- The current arises from photoelectrons emitted from the negative plate and collected at the positive plate



## Photoelectric Effect, Work Function

- Electrons ejected from the surface of the metal and not making collisions with other metal atoms before escaping possess the maximum kinetic energy  $K_{max}$
- $K_{\max} = hf \phi$   $\longrightarrow$  Einstein's idea
  - $\varphi$  is called the **work function**
  - The work function represents the minimum energy with which an electron is bound in the metal

## **Free-particle motion**

For a free particle,

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

**Dispersion relationship** 

### $E(k) \rightarrow Parabolic \ curve$

If the particle is an electron, then the E(k) relationship defines the electronic structures of the corresponding crystal material. We also call E(k) as energy band dispersion

## The electron shells of an atom



## Splitting of Energy Levels, final

- When this splitting is extended to the large number of atoms present in a solid, there is a large number of levels of varying energy
- These levels are so closely spaced they can be thought of as a **band** of energy levels



## Metals – Energy Bands

- At *T* = 0, the Fermi energy lies in the middle of the band
  - All levels below  $E_{\rm F}$  are filled and those above are empty
- If a potential difference is applied to the metal, electrons having energies near  $E_{\rm F}$  require only a small amount of additional energy from the applied field to reach nearby higher energy levels



## Semiconductors – Energy Bands

- Appreciable numbers of electrons are thermally excited into the conduction band
- A small applied potential difference can easily raise the energy of the electrons into the conduction band



## Insulator – Energy Bands

- The valence band is filled and the conduction band is empty at T = 0
- The Fermi energy lies somewhere in the energy gap
- At room temperature, very few electrons would be thermally excited into the conduction band



# The prototype Photoemission system back in1916



## Modern

### **PHOTOEMISSION SPECTROSCOPY**

Direct probing method of electronic states in materials



## Photoemission

- X-ray Photoemission spectroscopy (XPS)
   Photon energy > 100 eV
   Mainly looking at the localized Core level state
- 2. UV Photoemission spectroscopy (UPS)

Photon energy < 100 eV

Mainly looking at the delocalized and dispersive electronic state in the conduction and valence bands

# Energy range of the electrons sensitive to the surface



That is why photoemission is correlated to surface science

## The Principle of Photoemission → energy conservation





Scienta R3000 angle resolved photoemission station connected to BL03A HF-CGM beam line



Scienta R3000 angle resolved photoemission station connected to BL08A-LSGM beam line

XPS

## XPS Analysis of Pigment from Mummy Artwork



### The Photoelectric Process



 $\Phi$  = work function = energy to remove electron from fermi level to free vacuum/detector

### Auger Relation of Core Hole



Emitted Auger Electron

- L electron falls to fill core level vacancy (step 1).
- KLL Auger electron emitted to conserve energy released in step 1.
- The kinetic energy of the emitted Auger electron is:

KE = E(K) - E(L2) - E(L3).

XPS spectra of oxidised A1



### Adopted from lecture materials on line XPS spectra of oxidised A1



## Chemical shifts of the surface Use photon energy for depth probing



### Chemical shifts and why they exist

The core level binding energies are found to depend on the chemical state of the atom under investigation.



WHY?

Strange as the core levels do NOT

take part in the bonding

A simple (and not entirely sufficient) explanation :



Adopted from lecture materials on line

### XPS spectra for clean Al(100) Spin-orbit splitting and surface splitting



## UPS ------ ARPES

Angle-resolved Photoemission Spectroscopy

Mainly measuring the energy band dispersions of the electrons in valence level of crystalline solids

## **Energy versus momentum**

E(k) Direction is important !!!

# Energy band to energy band dispersions



Adopted from lecture materials on line (Eli Rotenberg)

### Three-step model for photoemission



## Momentum conservation and nonconservation through the inetrface



$$k_{\perp}^{out} = \sqrt{\frac{2mE_{kin}}{\hbar^2}} \cos \theta$$

$$k_{\parallel}^{out} = \sqrt{\frac{2mE_{kin}}{\hbar^2}} \sin \theta$$
Surface umklapp effect
$$k_{\parallel}^{out} = k_{f\parallel}^{in} = k_{i\parallel}^{in} + G_{//}$$
Final state effect
$$k_{\perp}^{out} \neq k_{f\perp}^{in} = k_{i\perp}^{in} + G_{\perp}$$

Through a free particle final band approximation

$$k_{f\perp}^{in} \approx \left(\frac{2m}{\hbar^2} (E_{kin} \cos^2 \theta + U_0)\right)^{1/2}$$

## In a crystal, the lattice undergoes a translational symmetry

$$\begin{split} \mathbf{T} &= u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 & \text{Translational vector in a real space} \\ n(\mathbf{r} + \mathbf{T}) &= n(\mathbf{r}) & \text{Electron number density} \\ n(x) &= n_0 + \sum_{p \geq 0} \left[ C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a) \right] & \text{1D case} \\ n(x + a) &= n_0 + \sum \left[ C_p \cos(2\pi p x/a + 2\pi p) + S_p \sin(2\pi p x/a + 2\pi p) \right] \\ &= n_0 + \sum \left[ C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a) \right] = n(x) & . \end{split}$$

$$n(\mathbf{x}) = \sum_{p} n_{p} \exp(i2\pi p\mathbf{x}/a)$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

$$\downarrow$$

$$In \ 1D \ case, \ real \ lattice \ a \qquad 3D \ case$$

$$reciprocal \ lattice \ 2\pi/a$$

### The reciprocal (k) lattice

construction of the reciprocal lattice

*Translational vector in a real space* 

 $T = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}$ 

*Translational vector in a reciprocal (k)space* 

$$\mathbf{G} = m'\mathbf{b_1} + n'\mathbf{b_2} + o'\mathbf{b_3}$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)}$$

a useful relation is

$$\mathbf{a}_i \mathbf{b}_j = 2\pi \delta_{ij}.$$

with this it is easy to see why

 $\mathbf{T} \cdot \mathbf{G} = 2\pi l$ 

In two dimensions





### Condition for diffraction in a crystal lattice



Effect of periodic potential is most dramatic on states of  $k = G_n/2$ (the boundaries of Brillouin zones): It opens energy *bandgaps* at  $k = G_n/2$  separating allowed *energy bands* 



Only need to consider states in 1<sup>st</sup> Brillouin zone Ag film



2D surface Brillouin zone constructed from LEED patterns of Ag films


Adapted from lecture materials on line Projection of bulk states in surface Brillouin zone



Zone center and zone boundaries are the symmetry points in the reciprocal space so the energy band dispersions <sup>3-D</sup> should be symmetry about these points.



#### Adopted from lecture materials on line True Surface States & Surface Resonances





*E. W. PLUMMER, W. EBERHARDT, Advances in Chemical Physics, Volume 49* 



 $k_{f\perp}^{in} = k_{i\perp}^{in} + G_{\perp} \longrightarrow$  Final state effect only for bulk state  $k_{f\parallel}^{in} = k_{i\parallel}^{in} + G_{\parallel} \longrightarrow$  Why not for 2D states?

# Photon energy dependence of the bulk and surface state ——>final

state\_effect



T. -C.Chiang, Surf. Sci. Rep. **39**, 181 (2000)  $k_{f\perp}^{in} = k_{i\perp}^{in} + G_{\perp} E_{kin} = \hbar \omega - \phi - E_{B}$ 

### Photoemission intensity

$$\begin{split} I(E_{kin}, \mathbf{k}_{\parallel}^{ext}, \hbar \omega) \propto \sum_{i, f, \mathbf{G}, \mathbf{g}_{\parallel}} & M_{fi}(\mathbf{k}_{f}, \mathbf{k}_{i}) \Big|^{2} \cdot \delta(E_{f} - E_{i} - \hbar \omega) \cdot \delta(\mathbf{k}_{f} - \mathbf{k}_{i} - \mathbf{G}) \\ & \text{Energy} & \text{Momentum} \\ & \text{Selection rule} & \text{conservation} & \text{conservation} \end{split}$$

$$\cdot \delta(E_{kin} + \Phi - E_f) \cdot \delta(\mathbf{k}_{\parallel}^{ext} - \mathbf{k}_{\parallel}^{int} - g_{\parallel})$$

Detection by energy analyzer *Momentum conservation parallel to surface* 

#### Photoemission and many body interactions

Photoemission intensity

$$I_{V}(E_{kin},k_{V\Pi}^{0}) \propto \sum_{f,i,\vec{G},\vec{g}\Pi} \left| \overline{M}_{fi}(\vec{k}_{f},\vec{k}_{i}) \right|^{2} \bullet (A_{h\omega} * A_{h})(E_{f} - E_{i} - \hbar\omega) \bullet L(\vec{k}_{f\perp} - \vec{k}_{i\perp} - \vec{G})$$
  

$$\bullet \delta(\vec{k}_{f\Pi} - \vec{k}_{i\Pi} - \vec{G}_{\Pi}) \bullet D_{E}(E_{kin} - E_{f} + \Phi) \bullet D_{k}(\vec{k}_{V\Pi} - \vec{k}_{f\Pi} - \vec{g}_{\Pi})$$
  
Surface Science Reports 30,153-206 (1998)  
Spectra function for the initial hole state
$$A(k,\omega) = \frac{|\text{Im}\Sigma(k,\omega)|}{[\omega - \varepsilon^{0}(k) - \text{Re}\Sigma(k,\omega)]^{2} + [\text{Im}\Sigma(k,\omega)]^{2}}$$
  
Spectra function is the form of a Lorentzian  
Quasiparticle picture

Sum rule  $\int_{-\infty}^{\infty} A(k,\omega) d\omega = 1$ 

# For a 2D system, we can make a lot of simplification

Peak intensity, peak position

 $v \sim w = \frac{2\pi e}{\hbar m c} \left| \left\langle \varphi_f \left| \vec{p} \right| \varphi_i \right\rangle \cdot \vec{A}_0 \right|^2 \delta \left( \varepsilon_f - \varepsilon_i - \hbar \omega \right) \right|$ Manv bodv interactions Line width , Line shape  $A(k,\omega) = \frac{\left|\operatorname{Im}\Sigma(k,\omega)\right|}{\left[\omega - \varepsilon^{0}(k) - \operatorname{Re}\Sigma(k,\omega)\right]^{2} + \left[\operatorname{Im}\Sigma(k,\omega)\right]^{2}}$ Spectra function for photohole Quasi particle Spectra function in the form of a Lorentzian

Photoemission intensity



Quasiparticle and quasihole are referred to as excited states induced by the many-body interactions



Adapted from lecture materials on line (Eli Rotenerg)

#### Symmetry selection rule

$\left M_{_{fl}} ight ^2\sim \left \left\langle oldsymbol{\psi}_f \left  {f A}\cdot {f p}  ight  oldsymbol{\psi}_i  ight angle  ight ^2$		
	Fixed by geometry	Sample- dependent

- The sample has mirror-plane symmetries.
- Each part of the matrix element has its own possible symmetry with respect to the sample plane.
- Whether a transition is allowed or forbidden depends on a combination of experimental geometry and the details of the wavefunctions



2001 Berkeley-Stanford Summer School

Adopted from lecture materials on line



#### Adopted from lecture materials on line (Eli Roternberg)



#### Only even initial states are observed at all rotation angles

#### Mixture of even and odd states

2001 Berkeley-Stanford Summer School

## We focus on 2D material sytems

Supposedly, there should be no final-state effect!

I will give examples to introduce five major aspects of photoemission spectra

- 1. Peak position
- 2. Peak intensity
- 3. Peak line width
- 4. Peak line shape
- 5. Energy band dispersions

# The electronic structures of 2D systems, metal surface and thin film

Ward Plummer

T.-C. Chiang



Surface States on Tungsten Phys. Rev. Lett. 25, 1493 (1970).



Quantum-Well States in a Metallic System: Ag on Au(111,Phys. Rev. Lett. 61, 1404 (1988) Observation of film states and surface-state precursor for Ag films on Si(111), Phys. Rev. B 33, 1460 (1986)

# Surface state and Quantum well state





## **Quantum well states**



**Bohr-Sommerfeld** quantization rule  $k_{\perp} = \frac{2n\pi - \phi_s(E) - \phi_i(E)}{2Nt}$  $E_n = E(k_\perp)$ **n**: Quantum number, 1,2,3,... N: the number of layers. **t** : the thickness of one layer  $\phi_{i+}\phi_{s}$  : interface and surface phase shift All the information of substrate bands are

embedded in  $\phi_i$ 

#### Surface state (SS)



FIG. 1. Schematic potential in the vicinity of a crystal surface. Surface states arise through multiple reflection between the terminating plane of the crystal and the surface barrier.

$$\phi \equiv \phi_C + \phi_B = 2\pi n$$
  
$$\phi_B / \pi = [(3.4 \text{ eV}) / (E_V - \epsilon)]^{1/2} - 1$$

N. V. Smith. PRB. 32, 3549 (1985)

Quantum well state (QWS)



Iwao. Matsuda *et al*. E-J. Surf. Sci. Nanotech. Vol. 2 (2004) 169-177

#### Quantum well state and surface states within the energy gap



PRB 36, 5809, 1987

#### Metal surfaces and metal thin films



## Peak position

(Thickness dependence of thin films)



Surface states: Due to the interaction with the substrate when the decay length of the surface state is longer than thickness. The decay length can be extracted from the thicknessdependent energy shift . Phys. Rev. B 65, 125319 (2002) Phys. Rev. Lett. 55, 2483 (1985)

Quantum well states: Due to quantum size effects governed by Bohr-Sommerfeld quantization rule. The phase shift at the interface can be extracted from the thicknessdependent Energy shift.

## Peak position



Temperature dependence of surface state peak position indicates the surface thermal expansion behavior

### Peak position (Adsorption dependence)



Adsorption dependence of SS peak position determines the type of adsorption, chemisorptions (charge transfer) or physisorption (van der waals forces).

## Peak position

#### (Adsorption dependence)



# Peak intensity (photon-energy dependence)



Photon energy dependence of the surface state peak intensity determines the surface state decay length



*Temperature dependence of SS and QWS peak intensity determines the Debye temperature via Debye- Waller factor* 

## Peak intensity

### (Temperature dependence of thin films)



QWS as the indicator of Thermal stability of thin films

### **Peak linewidth**

$$\begin{aligned} & \text{Spectral function} \quad A(k,\omega) = \frac{\left|\text{Im}\,\Sigma(k,\omega)\right|}{\left[\omega - \varepsilon^{0}(k) - \text{Re}\,\Sigma(k,\omega)\right]^{2} + \left[\text{Im}\,\Sigma(k,\omega)\right]^{2}} \\ & \text{Im}\,\Sigma(\omega,T) \Rightarrow \text{ peak width} \Rightarrow \text{surface state hole life time} \Rightarrow \text{electron-phonon interaction} \\ & \text{electron-electron interaction} \\ & \text{electron-electron interaction} \\ & \text{surface defect scattering} \\ & \text{Im}\,\Sigma_{ep}(\omega,T) = \frac{\hbar}{\tau} = 2\pi\hbar\int_{0}^{\omega_{max}} \alpha^{2}F(\omega)[1 - f(\omega - \omega) + 2n(\omega) + f(\omega + \omega)]d\omega \end{aligned}$$

$$\begin{aligned} & \text{Eliashberg coupling function} \\ & \text{to represent phonon densities} \\ & \sigma^{2}F(\omega) = \lambda\left(\frac{\omega}{\omega_{D}}\right)^{2} \text{ if } \omega < \omega_{D} \\ & \text{when} \quad T < \frac{\hbar\omega_{D}}{k_{B}} \quad \text{Im}\,\Sigma_{ep}(\omega,T) \propto T^{3} \\ & \text{when} \quad T > \frac{\hbar\omega_{D}}{k_{B}} \quad \text{Im}\,\Sigma_{ep}(\omega,T) \approx 2k_{B}T\lambda\pi \\ & \alpha^{2}F(\omega) = \frac{\lambda\omega_{E}}{2}\delta(\omega - \omega_{E}) \end{aligned}$$

#### Temperature dependence of S1 and S2 surface states at $\,A$



## Extracting EP coupling strength



Einstein model fitting results  $\omega_E = 64meV$   $\lambda_{S1} = 0.646 \pm 0.02$  $(\lambda_{bulk} = 0.24 \pm 0.05)$ 

Debye model fitting results

 $\omega_{D} = 60 meV$  $\lambda_{S2} = 0.491 \pm 0.04$ 

 $(\lambda_{\rm bulk}=0.24\pm0.05)$ 

## Peak lineshape → layer resolution

Normally, the sharp and intense lineshapes of SS and QWS indicate the smooth surfaces and uniform thin films. They can further reveal the layer reolutison



# Atomically uniform + quantum size effect



Thickness changes (uniform films)
The allowed quantized k<sub>⊥</sub>'s changes
The energy positions of the QWS changes
Properties of films change

Surface energy, work function, thermal stability, adsorption, superconductivity transition temperature, magnetic interlayer coupling......



#### Peak lineshape → layer resolution



Layer resolution revealed by the lineshape of surface state of Ag films on Au(111)

APPLIED PHYSICS LETTERS **92,** 163102 2008

## Peak lineshape→ many body interactions

$$A(k,\omega) = \frac{\left|\operatorname{Im}\Sigma(k,\omega)\right|}{\left[\omega - \varepsilon^{0}(k) - \operatorname{Re}\Sigma(k,\omega)\right]^{2} + \left[\operatorname{Im}\Sigma(k,\omega)\right]^{2}}$$

Quasi-particle (typical): One state → Lorenzian shape

Non Quasi-particle behavior (special): One state -> Non-Lorenzian shape

The lineshape for the layer resolution shown before are composed of two states of two Lorenzian shapes.

### Electronic phonon coupling of surface states

Re  $\Sigma_{ep}(\omega,T) \rightarrow$ The shift of the hole state energy from the ground state energy due to the many body interaction

- → Relevant only near Fermi surface within the maxmium phonon energy range
- → Ionic screening causing renormalized hole state velocity or effective mass  $m^* = (1 + \lambda)m$

Surface state band distortion on crossing phonon energies


#### Peak lineshape→ many body interactions→ electron phonon interaction



PRB 60, 10796 (1999)

PRB 61, 2371 (2000)



Different lineshapes to reveal coupling to different optical phonon energies  $\hbar \omega^{H} = 161$  meV,  $\hbar \omega^{D} = 117$  meV.



Debye model ( $\hbar\omega_D = 70meV$ ) for Be(0001) and Einstein model ( $\hbar\omega_E = 64meV$ ) for Be(1010)

#### Peak lineshape → many body interactions → electron electron interaction



The two-peak line shape across the substrate band edge is non quasiparticle

Retarded Green function for a single electron state entering into the bulk band continuum.

$$G(E)^{\!-\!1} = E - E_q + i \delta_q - \int_{\scriptscriptstyle -\infty}^{E_0} \! rac{\left|V
ight|^2}{E - arepsilon + i \delta_s} g(arepsilon) darepsilon$$

 $g(\varepsilon) = \frac{A}{\sqrt{E_0 - \varepsilon}} \Theta(E_0 - \varepsilon) \quad \begin{array}{l} \text{One dimensional form of} \\ \text{the density of the states} \\ \text{for the substrate band} \\ \text{Spectral function} \\ A(E) - \frac{1}{\pi} \operatorname{Im}(G) = -\frac{1}{\pi} \operatorname{Im} \left( \frac{1}{E - E_q + i\delta_q - \pi A |V|^2 (E - E_0 + i\delta_s)^{-1/2}} \right) \end{array}$ 

Phys. Rev. Lett. 93, 216804 (2004)

## Ag films on Ge(111)



## Band dispersions $\rightarrow$ Layer resolution



## Band dispersions→ electron-phonon interactions



For more information regarding using MDCs to extract self –energies, please check Science **285**, 2110 (1999)

## $Be(10\overline{1}0)$ : Real part of self-energy

Real part



Online material: https://web2.ph.utexas.edu/~jrshi/VAS11.pdf

#### Band dispersions $\rightarrow$ electron-electron interactions

Strong e-e interaction between Pb QWS subbands and Ge band edges



# The electron-electron interaction model for film 2ML

The density of states of QWS is dominated by the Ge bulk band edges so we can simply use the density of state model to do the fitting

Spectra function

$$A(E) \propto \left| \langle QWS | V | bandedges \rangle \right|^2 g(E) = \left| M \right|^2 g(E) \xrightarrow{g(E) \sim \int dk \delta(\varepsilon_f - \varepsilon_i)}{g(E) \sim \int dk A(k, \varepsilon_i)}$$

density of states (1D form) — At each K point



## The electron-electron interaction model for film > 2ML

By using Anderson's model for the electron-electron interaction between the discrete states and continuous states, we do the fitting.

retarded Green's function

$$G(E)^{-1} = E - E_q + i\delta_q - \sum_{i=1}^{3} \int_{-\infty}^{E_0^i} \frac{|V_i|^2}{E - \varepsilon + i\delta_s^i} g_i(\varepsilon) d\varepsilon$$

density of states

 $g_i(\varepsilon) = \frac{A_i}{\sqrt{E_0^i - \varepsilon}} \Theta(E_0^i - \varepsilon)$  For HH, LH and SO band edges of bulk Ge

spectral function

$$A(E) = -\frac{1}{\pi} \operatorname{Im}(G) = -\frac{1}{\pi} \operatorname{Im}\left(\frac{1}{E - E_q + i\delta_q - \sum_{i=1}^3 \pi A_i |V_i|^2 (E - E_0^i + i\delta_s^i)^{-1/2}}\right)$$

 $|V_i| = \langle QWS | V_i | bandedges \rangle$ 



Phys. Rev. Lett. 107, 066802 (2011)

Electron-electron interaction becomes the driving force for the growth of Pb films in (1x1) configuartion



Electronic match versus Lattice match

#### Band dispersions $\rightarrow$ electron-electron interactions



Figure 1 | Photoemission data for CuPc on Ag thin films on Ge(111). (a) Normal emission spectra as a function of CuPc coverage for 10-ML Ag thin film on Ge(111). (b) Angle-resolved photoemission result along  $\overline{TM}$  for 10-ML Ag thin film on Ge(111). (c) Angle-resolved photoemission result along  $\overline{TM}$  for 10-ML Ag thin film on Ge(111). (c) Angle-resolved photoemission result along  $\overline{TM}$  for 1-ML CuPc on 10-ML Ag thin film on Ge(111). (d) Vacuum-level shift as a function of CuPc coverage for 7-, 10- and 12-ML Ag thin films. (e) Normal emission spectra for 1-ML CuPc on 7-, 10- and 12-ML Ag thin films. The black wedges indicate the energy positions of the gap states.

#### Newns-Anderson model to explain the adsorption induced Gap state

Nature Communications 4, 2925 (2013)





## Band dispersions $\rightarrow$ effects from the unklampp scattering at the interface



 $(k_{1\perp} + k_{2\perp} + k_{3\perp} + k_{4\perp}) * d + \phi = 2\pi n, n = 1, 2, 3, 4$   $(k_{1\perp}(E_1) + k_{2\perp}(E_2) + k_{3\perp}(E_3) + k_{4\perp}(E_4)) * d + \phi = 2\pi n$ Due to energy conservation  $(k_{1\perp}(E) + k_{2\perp}(E) + k_{3\perp}(E) + k_{4\perp}(E)) * d + \phi = 2\pi n$  $K_{\perp}^{NEW}(E) d + \phi = 2\pi n$ 

,d= Nt , t=2.36 Å for 1ML of Ag in (111) direction

Phys. Rev. Lett. 96, 216803 (2006)



Substrate



The Ge substrate working as a diffraction grating

$$\vec{K}_{\|-\overline{M}} = \vec{K}_{\|\overline{M}} - \vec{G}_{\|} \qquad \vec{G}_{\|} = 2\vec{K}_{\|\overline{M}}$$

## Substrate is the key



## Band dispersions $\rightarrow$ hybridization $\rightarrow$ anti-crossing



$$\widehat{H} = \begin{bmatrix} E_1(k) & V \\ V & E_2(k) \end{bmatrix}$$

*E*<sub>1</sub>(*k*),*E*<sub>2</sub>(*k*) → The two original energy band dispersions before hybridization interaction *V* → The hybridization interaction

matrix elements

Au particles adsorbed on Ag/Si(111)- $\sqrt{3} \times \sqrt{3}R30^{\circ}$  surface

PRL 96, 036803 (2006)

#### Varied hybridizations from metal surfaces and metal thin films





### Band dispersions → Rashba effect

- 1. Strong spin-orbital coupling
- 2. Breaking of the inversion symmetry with time-reversal symmetry preserved → out-of-plane potential gradient

 $E(k_{//} f) = E(-k_{//} 4)$ 

- 3. Heavy-metal crystal surfaces, Au(111), Bi(111), Bi(100), W(110)...
- 4. Heavy-metal ultra thin films on semiconductors, Bi/Si(111), Tl/Si(111),  $Pb/Ge(111) \sqrt{3} \times \sqrt{3} R30^{\circ}$ ,  $Bi/Ge(111) \sqrt{3} \times \sqrt{3} R30^{\circ}$ , and  $Au/Ge(111) \sqrt{3} \times \sqrt{3} R30^{\circ}$ .....
- 5. Heavy-and-light-element alloys on metal surfaces BiAg, PbAg, SnAg alloys on Ag(111) →In-plane potential gradient
- 6. Heavy-and-heavy-element alloy on semiconductor surfaces , PbAu alloy.

#### Spin-orbital coupling for 2D free electron gas

Assume no crystal potential in k<sub>1</sub> direction  $\hat{H} = \frac{k_{\parallel}^2}{2m} + \alpha_R \vec{\sigma} \cdot (\vec{k}_{\parallel} \times \hat{z}) \qquad \vec{k}_{\parallel} = k_x \hat{i} + k_y \hat{j}$ The corresponding  $E_{\pm} = \frac{\hbar^2 k_{\parallel}^2}{2m} \pm \alpha_R k_{\parallel} = \frac{\hbar^2}{2m} (k_{\parallel} \pm k_0)^2 - \Delta_0$ eigenvalues are  $\mathbf{k}_{\parallel} = \sqrt{\mathbf{k}_x^2 + \mathbf{k}_y^2} \quad \mathbf{k}_0 = \frac{\mathbf{m}\alpha_R}{\hbar^2} \qquad \text{One way to determine} \\ \text{the Rashba parameter}$ α  $\Delta_0 = (\alpha_R m / \hbar^2)$  $E_{R} = \frac{\hbar^{2}k_{0}^{2}}{2m} \rightarrow \alpha_{R} = \frac{2E_{R}}{k_{0}} \rightarrow Another way to determine the Rashba parameter \alpha$ Rashba parameter  $\alpha$  $\Delta E = E_+ - E_- = 2 \alpha_R k_{II}$  The third way to determine the Rashba parameter  $\alpha$ 



Au(111)



M. Hoesch et al., Phys. Rev. B 69, 241401(R) (2004)

# Large Rashba splitting for Pb/Si(111)- $\sqrt{3}$ R30



Nature Commun. 1, 17 (2010).

#### Isotopic and anisotropic Rashba splitting



In-plane Inversion symmetry breaking along horizontal mirror plane

### Rashba +Hybridization



Phys. Rev. Lett. 101, 107604 (2008)



### Rashba +Hybridyzation



New J. Phys. 16, 045003 (2014)

#### Electronic structures of PbAu alloy with one-layer capping Au (T = RT)



## Matrix element effect for the coupling of the orbital symmetry with beam polarization

• PbAu alloy film





#### Above all, observation and imagination with an excessively optimistic and curious mind is the most important key!!!



*Pb fiim on Au/Ge(111)-Root3* 

PbAu alolly /Pb fiim/Ge(111)-Root3

## Conclusion

What I introduced are only based on my past researches on various surface and thin-film systems. The research fields and materials systems that photoemission have been employed to study are too large and too many. Nevertheless, I hope some ideas I pass to you for extracting physics from the photoemission data can be helpful for your future researches.