Angle-resolved photoemission spectroscopy on emergent quantum materials

Part -1

Outline

- Introduction to angle-resolved photoemission spectroscopy (ARPES)
 - The principle of ARPES
 - Current status of ARPES beamline at NSRRC

• The electronic structure of emergent materials

- Surface states and quantum well states
- Graphene based materials
- Beyond graphene : 2D materials
- Topological insulators (TIs)
- Toward future electronic devices

Summary

What is photoemission?



Photon in -> electron out (emission)

What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)



Initial state: ground (neutral) state

Conservation of energy

 E_k : photoelectron kinetic energy $E_i(N)$: total initial state system energy $E_f(N-1)$: total final state system energy Electron energy analyzer



Final state: hole (excited) state



Energy Distribution Curve (EDC) (Spectrum)

The energy level of hydrogen atom





Kyle Shen, IGERT Lecture 2008



The crystal structure and momentum space



primitive vectors **a**₁, **a**₂, **a**₃

reciprocal lattice vector **b**₁,**b**₂,**b**₃



$$\vec{b}_{1} = 2\pi \frac{\vec{a}_{2} \times \vec{a}_{3}}{V}$$
$$\vec{b}_{2} = 2\pi \frac{\vec{a}_{3} \times \vec{a}_{1}}{V}$$
$$\vec{b}_{3} = 2\pi \frac{\vec{a}_{1} \times \vec{a}_{2}}{V}$$
$$V = \vec{a}_{1} \cdot \vec{a}_{2} \times \vec{a}_{3}$$
reciprocal lattice **G** :
$$\vec{G} = l\vec{b}_{1} + m\vec{b}_{2} + n\vec{b}_{3}$$
l,m,n are any integers

 \vec{G}

- Deeply bound "core" electrons remain basically unchanged
- Outermost "valence" electrons hybridize forming continuous "energy bands"



Band theory

Two approximations

Nearly free electrons. Electrons are non-interacting in a periodic crystal potential which is relatively weak and can be treated as a perturbation. As in the free-electron-gas model, they are still subject to the Pauli exclusion principle.

Free electron gas : The interactions between electrons and between electrons and nuclei are turned off, subject only to the Pauli exclusion principle.

Tightly-bonding approximation

Electrons are tightly bound to particular atoms, overlapping only weakly with neighbors.

Fermi-Dirac Distribution

Thermal Properties of Free Electron Gas: Almost every electronic transport property of solids is proportional to $D(\mathcal{E}_F)$.

Fermi function
(Fermi-Dirac distribution)
$$f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/k_BT} + 1}$$
RT ~ 25 meV
$$f(\mathcal{E}): k_BT = .005\mu$$

$$f(\mathcal{E}): k_BT = .025\mu$$

$$exp[-\beta(\mathcal{E}-\mu)]: k_BT = .25\mu$$

$$\mu$$



Fig. 2.3. Ultra-high resolution photoemission spectrum on a polycrystalline gold sample (evaporated Au film) for the determination of the energy resolution. The Fermi edge was measured at T = 2.9 K using a frequency tripled (KBe₂BO₃F₂ crystal, KBBF) YVO₃ laser for the photoexcitation ($h\nu = 6.994$ eV) [15]

Hufner, Very high resolution photoelectron spectroscopy

Why ARPES - key technique for the electronic structure mapping

- Angle-resolved photoemission spectroscopy (ARPES) is the most general tool to probe band structure, electronic interactions or spectral function mapping.
- Broad applications: surfaces, thin films, bulk materials, superconductors, magnetic/spin systems, complex materials, topological insulators, graphene based materials, charge density wave materials, low-dimensional systems, artificial stacks, device configurations, etc.



The unit cell of graphene



$$H(\vec{k}) = \begin{pmatrix} E_0 + \Delta & \gamma_0 f(\vec{k}) & \gamma_1 & \gamma_4 f^*(\vec{k}) \\ \gamma_0 f^*(\vec{k}) & E_0 & \gamma_4 f^*(\vec{k}) & \gamma_3 f(\vec{k}) \\ \gamma_1 & \gamma_4 f(\vec{k}) & E_0 + \Delta & \gamma_0 f^*(\vec{k}) \\ \gamma_4 f(\vec{k}) & \gamma_3 f^*(\vec{k}) & \gamma_0 f(\vec{k}) & E_0 \end{pmatrix}$$
(b)

$$f(\vec{k}) = \exp(ik_x a_0 / 2\sqrt{3}) + 2\exp(-ik_x a_0 / 2\sqrt{3})\cos(k_y / 2)$$
$$\vec{k} = (k_x, k_y)$$

A. Gruneis et al., PRB (2008)

Pure 2D material : graphene









Coletti et al., PRB (2013)



The band structure of graphene





Constant energy mapping



Coletti et al., PRB (2013)

Fermi Surface



Why orientation of solid so important



conventional ARPES of polycrystalline graphite

Fermi Surface

most of the momentum information is lost as our spot size is much larger than the grain size.

How to probe the electronic structure of solids

Angular Resolved Photoemission Spectroscopy(ARPES)



Electron emission angle: Θ Photon incident angle: ψ , *s*- and *p*-polarization

$$k_{\prime\prime\prime} = \sqrt{\frac{2m}{\hbar^2}} E_k \cdot \sin\theta$$
$$k_{\prime\prime}(\text{Å}^{-1}) = 0.5123\sqrt{E_k(eV)} \cdot \sin\theta$$

 $k_{\parallel}(\text{inside}) = k_{\parallel}(\text{outside})$

Conservation of liner momentum

Important for 3D and 2D band mapping

$$k_{\perp} = 0.5123 \sqrt{(E_{kin} \cos^2 \theta + V_0)}$$

Conservation of linear momentum parallel to the surface



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2}} E_{kin}$$
$$k_{in} = \sqrt{\frac{2m}{\hbar^2}} (E_{kin} + V_0)$$
$$k_{out,\parallel} = k_{in,\parallel} \equiv k_{\parallel}$$

"Snell's Law"

$$k_{\parallel} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2}} E_{kin} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2}} (E_{kin} + V_0)$$

Critical angle for emission

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$



$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$
$$k_{\prime\prime} = 0.5123\sqrt{E_{kin}}\sin\theta$$



- Low photon energy provides better momentum resolution, but the covering range of BZ is also small.
- We expect to study the electronic structure of solids at VUV region (10 eV~ 100 eV).



Krempasky et al., JESRP (2010)

$$k_{\perp} = 0.5123 \sqrt{(E_{kin} \cos^2 \theta + V_0)}$$

$$k_{//} = 0.5123 \sqrt{E_{kin}} \sin \theta$$

Lattice constant : Graphene : 2.46 Å Cu(111) : 2.08 Å MoS_2 : 3.12 Å

Assume the work function is 4.3 eV, please estimate the largest covering range of BZ at the Fermi level at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy.
 Answer: 0.67 Å⁻¹, 2.11 Å⁻¹, 3.46 Å⁻¹, 5.01 Å⁻¹, 11.4 Å⁻¹

- ✓ The angle between the incident beam and spectrometer is 50 degree, please estimate the covering range of BZ at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy.
 Answer: 0.51 Å⁻¹, 1.61 Å⁻¹, 2.65 Å⁻¹, 3.83 Å⁻¹, 8.45 Å⁻¹
- The BZ in single layer graphene, the magnitude of FK is 1.703 Å⁻¹. If you plan to probe the band structure of graphene near the K-point, what are the required angle between the surface normal and spectrometer at 6 eV, 21.2 eV, 50 eV, 100 eV and 500 eV photon energy?
 Answer: mission impossible, 54 degree, 29.5 degree, 19.9 degree, 8.6 degree



Figure 3. Angleresolved photoemission spectra of the Shockley surface state and a series of quantum well of 40 states ML Ag/Cu(111) recorded at photon energies of 6 eV (fourth harmonic of the Ti:sapphire oscillator, 4(a)) and 21.22 eV (He I line of a discharge lamp, VUV 4(b)), respectively.

S Mathias et al., J. Physics : Conference series (2009)

> You need to understand the crystal structure of solids.

- The sample characterization, such as the orientation and crystalline, is quite important before the experiment.
- > XRD, Laue diffraction and LEED are required.

Energy scale and important excitations



- ➤Superconducting gap ~ 1 100meV
- ➢Optical Phonons: ~ 40 200 meV
- Magnons: ~ 10 meV 40 meV
- Pseudogap ~ 30-300 meV
- Multiphonons and multimagnons ~ 50-500 meV
- Orbital fluctuations (originated from optically forbidden *d-d* excitations): ~ 100 meV 1.5 eV

Requirement: High Energy Resolution with High Intensity

Z. Hussain, ALS summer school

Superconducting gap



Hufner, Very high resolution photoelectron spectroscopy

Light sources and terminology

- Ultraviolet Photoemission Spectroscopy (UPS)
 - UV He lamp (21.2 eV, 40.8 eV)
 - Laser : 6 eV (BBO), 8 eV (KBBF), 11 eV (gas cell) or HHG (High harmonic generation)
 - Valence band PES, direct electronic state info.
- X-ray Photoemission Spectroscopy (XPS)

(Electron Spectroscopy for Chemical Analysis) (ESCA)

- X-ray gun (Al: 1486.6 eV, Mg: 1253.6 eV)
- core level PE, indirect electronic state info
- chemical analysis

Synchrotron radiation

- continuous tunable wavelength
- valance band and core level

Current status of ARPES end station at TLS


- typical energy resolution ~ 0.1 to 0.01 eV.
 Best systems are ~ 0.001 eV.
- most electron analyzers operate using electrostatic optics (magnetic fields harder to control)
- detectors are typically channel plates (electron multipliers) with a CCD or current pulse output

 detecting & manipulating electrons is relatively easy



Kyle Shen, IGERT Lecture 2008





Kyle Shen, IGERT Lecture 2008

Early ARPES experimental result







FIG. 1. Angle-resolved photoemission spectra taken using 22-eV photon energy, at room temperature, for photon electric field (a) parallel and (b) perpendicular to the conducting axis. The emission angle is along the conducting axis, with the surface normal defined as 0° .

Now a 2-D detector with \pm 30° and 0.1° angular resolution can be obtained.

FIG. 1. A series of high-energy-resolution angle-resolved photoemission spectra, taken along the direction of the sample and for different values of the azimuthal angle.

SCIENTA R4000 Side View





- Angle-resolved spectrometers collects electrons as a function of kinetic energy and emission angle
- Due to the slit, only angles along one axis (q_x) can be detected simultaneously



Constant energy mapping for ARPES Scan

- Deflection can also be done in θ_v
- This enables full cone detection, $0 < \theta < 15^{\circ}$, without sample rotation



Angle is the soul of ARPES: Band mapping



Experimental geometry



Eli Rotenberg, ALS summer school

Typical Experimental Result

Accumulate spectra of Rashba effect on Au(111) as the angle is scanned Emission



Au(111) : The inversion symmetry is broken at the surface



In a nearly free electron picture, $\vec{\nabla}V$ is perpendicular to the surface



two spin polarized SS bands



Surface state of Au(111)



Rashba effect on Au(111)



Deflector analyser

- With the deflector analyser, the electron trajectories can be deflected, to change the range of emission angles that reaches the detector
- Deflection can be done in q_x and in q_y .



Graphite



Data courtesy : Dr. Yamane, IMS

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www.vgscienta.com⁵¹

The Fermi surface of Bi(111)



Why are electrons so useful as probes of surfaces?

Or

Not so useful for studying bulk properties !! Minimum due to electron-electron scattering, mainly plasmons PES is a surface sensitive technique! (requires UHV) High energy photoemission: several keV to increase bulk sensitivity



The requirement of ARPES

- UHV environment : better than 1x10⁻¹⁰ Torr
- Single crystals or *in-situ* growth thin films
- Conductors or semiconductors
- Tunable photon energies





Figure 5.2: (color) The oxygen 1s peaks from Bi2212 at different times after the cleave. A constant background was subtracted from each spectrum to allow direct comparison. The peak derived from bulk oxygen is stable over time, while the surface oxygen peak grows as more oxygen sticks to the cold surface.

HC Hsu, Ph.D. Thesis NTNU(2010) Koralek, U. Colorado Ph.D. Thesis (2007)

Single crystals or *in-situ* growth well-ordered thin films are favorable for ARPES measurement



Base pressure : 1x10⁻¹⁰ Torr In-situ cleaved Bi₂Se₃ single crystal

Park et al., PRB (2010)

Using ARPES to study the electronic structure of 2D materials

Surface state



Surface states are highly localized in real space, therefore completely delocalized in k-space along kz. – NO DISPERSION OF SURFACE STATES in kz direction

Eli Rotenberg, ALS summer school

• Surface = Breakdown of the translational symmetry

 \Rightarrow Peculiar solution in the gap with a complexe wave vector k_[111]



→localisation of the electronic density at the surface Surf. State is very sensitive to any structural modification

Quantum well states



Ag(111) thin films expitaxially grown on Au(111) substrate



Quantized discretely along z-direction Energy levels depend on film thickness L

Nearly free electron like in xy-plane

Bulk projected bands along ΓL of Au and Ag, respectively

Absolute coverage of thin films : Ag/Au(111) system



Dynamically monitor the thin film growth mechanism



FIG. 2. Energy distribution curves of normal emission from Ag (22 ML) on Au(111) annealed at the indicated temperatures; intensities have been scaled variously for stacking presentation.







D.-A. Luh et al., PRB (2008)

The examination of 2D behavior



Cheng et al., submitted to PRB

The examination of 2D behavior : tuning incident photon energy



2D materials – An Overview

The most well-known 2D material : Graphene

- \checkmark First 2D materials studied in detail.
- \checkmark Became famous by the works of Novolesov & Geim since 2004.
- ✓ High mobilities (> 100,000 cm2/Vs at RT) raised expectations in future electronic devices.
- ✓ Significant attention for 2D materials beyond graphene

The strictly two-dimensional material

- 70 years ago, Landau argued that strictly 2D crystals were thermodynamically unstable and could not exist
- Before 2004, atomic monolayers only as integral part of 3D structure, grown epitaxially on top of monocrystal
- The discovery of graphene and other free-standing 2D atomic crystals (ex :single layer boron nitride and half-layer BSCCO)

New inroads into low-dimensional physics New surprise to provide highly potential for application

Charge transfer process on ML C₆₀/Cu(111) system



- 1. Large 7-atom vacancies.
- 2. Significant top Cu layer coherent distortion.
- Nearly "optimal" C₆₀³⁻ doping purely by interface reconstruction.



Ref: W.W. Pai et al., PRL 104, 036103 (2010)

What Is Graphene









What is graphene



How to distinguish the thickness of graphene



Optical microscopy



B. özyilmaz , NUS, Singapore

Raman spectroscopy



A. Ferrari, PRL 97,187401 (2006)

Single layer and bilayer graphene




Metrological applications



Novoselov et al., Nature (2012)

First treament: graphite



The experiments in graphene on SiO₂ (200nm) and suspended graphene



PRB 84, 115401 (2011)

Nano-XPS results on exfoliated graphene samples on SiO₂ substrates at the ANTARES beamline, SOLEIL



Avila, Synchrotron Radiation News (2014)

CVD for large scale graphene film





Figure 3 | Transfer processes for large-scale graphene films. a, A

Kim et al., Nature (2009)

Graphene formation by decomposition of C₆₀







Perdigao et al., J. Physical Chemistry C (2011)

Epitaxial growth graphene on SiC



The electronic structure of bilayer graphene on SiC substrate



Cheng et al., submitted to PRB

A intrinsic gap exists or not?



Figure 1 Schematic representation of crystal and electronic band structures (only π -bands are shown). **a**, Free-standing graphene. **b**, Boron-nitride. **c**, Epitaxial graphene. Symmetry between the sublattices in graphene guarantees gapless spectra around *K* points. This symmetry is broken in boron-nitride (one sublattice consists of boron atoms, another of nitrogen), which immediately opens a gap. In epitaxial graphene, the commensurate underlying potential gives rise to different on-site energies for the two sublattices, which opens a small gap around *K* points.

Novoselov, Nature Mat. (2007)