ANGLE-RESOLVED PHOTOEMISSION STUDIES OF TWO-DIMENSIONAL ELECTRON SYSTEMS

BY

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DISSERTATION

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Abstract

This dissertation examines the electronic properties of 2D electron systems, including ultrathin metallic films grown on semiconductor substrates and graphite/graphene layers. Both systems are (quasi) two-dimensional and are of particular interest due to their technological importance. The major experimental tool is angle-resolved photoemission spectroscopy, which can directly measure the spectral function of the quasiparticle.

The study of ultrathin metallic films focuses on the substrate effect on the electronic structure of the film. Thin metallic films can support quantum well states, which are essentially electronic standing waves. Our work on Ag films grown on Ge(111) demonstrates that the incommensurate interface potential results in strong modifications to quantum well states. The observed electronic interference structures are attributable to the mixing of electronic standing waves by the Ag-Ge interface potential. The complex Fermi surface, as a result of this interface scattering, can affect the electronic transport properties.

An even stronger modification of quantum well states can be observed when the metal films are grown on stepped substrates. More specifically, our study of corrugated Ag/Pb films grown on Si(557)-Au surface reveals multiple sets of quantum well states that are centered at the Brillouin zone boundaries corresponding to the step modulation. This indicates that the valence electrons form coherent grating cavity modes which are defined by the corrugation geometry.

Graphitic materials, made of sheets of carbon atomic layers, have unusual electronic structures known as Dirac cones. Our photoemission measurements of graphite/graphene layers reveal unexpected gaps at normal emission, one at ~67 meV and another much weaker one at ~150 meV. The major gap features persist up to room temperature, and diminish with increasing emission angles. We show that these gaps arise from electronic coupling to out-of-plane and in-plane vibrational modes at the $\bar{K}$ point, respectively, in accordance with conservation laws and selection rules governed by quantum mechanics. Our study suggests a new approach for characterizing phonons and electron-phonon coupling in solids.
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# Table of Contents

List of Abbreviations ................................................................. vii  
List of Symbols ............................................................... viii  

1 Introduction .......................................................... 1  
1.1 Substrate Effects on Quantum Well States ......................... 1  
1.2 Electron-Phonon Coupling in Graphite/Graphene ...................... 3  
1.3 Thesis Overview .................................................... 5  
   References .......................................................... 5  
   Figures .......................................................... 7  

2 Angle-Resolved Photoemission Spectroscopy ....................... 9  
2.1 Overview .......................................................... 9  
2.2 A Simple View of Photoemission Process ......................... 9  
2.3 Preparation for ARPES Experiment .................................. 11  
   2.3.1 Ultrahigh Vacuum ............................................. 11  
   2.3.2 In-Situ Sample Preparation ................................. 13  
   2.3.3 Sample Characterization ..................................... 14  
2.4 ARPES Apparatus .................................................. 15  
   2.4.1 Light Source ................................................ 15  
   2.4.2 Electron Analyzer .......................................... 16  
2.5 Photoemission Theory ............................................. 18  
   2.5.1 Photon Energy Dependence ................................. 22  
   2.5.2 Surface Transition .......................................... 23  
   References .......................................................... 23  
   Figures .......................................................... 25  

3 Theoretical Backgrounds ............................................. 33
3.1 Introduction .................................................. 33
3.2 Quantum Well States ........................................... 33
  3.2.1 QWS in Freestanding Films ............................... 35
  3.2.2 QWS in Metallic Films on Semiconductor Substrates .......... 36
  3.2.3 QWS vs Surface State .................................. 37
3.3 Electron-Phonon Coupling .................................... 39
  3.3.1 Electron-Phonon Scattering Matrix Element .................. 39
  3.3.2 Measuring e-ph Coupling by ARPES ........................ 44
References ......................................................... 45
Figures ............................................................ 47

4 Interface-Induced Interference in Ag/Ge(111) ...................... 54
  4.1 Introduction .................................................. 54
  4.2 Previous Studies ............................................ 54
  4.3 Three-Dimensional Band Structure Mapping ..................... 55
  4.4 Interface-Induced Electronic Interference Structures ............ 56
  4.5 Thickness Dependence Study ................................ 58
  4.6 Conclusions .................................................. 59
    References ..................................................... 60
    Figures ........................................................ 61

5 Coherent Grating Cavity Modes in Corrugated Films ................. 68
  5.1 Introduction .................................................. 68
  5.2 One-Dimensional vs Two-Dimensional .......................... 69
  5.3 Ag Films on Si(557)-Au ...................................... 71
  5.4 Pb Films on Si(557)-Au ...................................... 73
  5.5 Coherent Grating Cavity Modes ............................... 74
  5.6 Blazed Diffraction of Final State ............................. 77
  5.7 Conclusions and Outlook .................................... 78
    References ..................................................... 79
    Figures ........................................................ 81
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D, 2D, 3D</td>
<td>One-, Two-, Three-Dimensional</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-Resolved Photoemission Spectroscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
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<tr>
<td>Ge</td>
<td>Germanium</td>
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<tr>
<td>Pb</td>
<td>Lead</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
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<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>QWS</td>
<td>Quantum Well State</td>
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<tr>
<td>ML</td>
<td>Monolayer</td>
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<tr>
<td>e-ph</td>
<td>Electron-Phonon</td>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>LEED</td>
<td>Low-Energy Electron Diffraction</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High-Energy Electron Diffraction</td>
</tr>
<tr>
<td>SRC</td>
<td>Synchrotron Radiation Center</td>
</tr>
<tr>
<td>EDC</td>
<td>Energy Distribution Curve</td>
</tr>
<tr>
<td>MDC</td>
<td>Momentum Distribution Curve</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of State</td>
</tr>
<tr>
<td>SS</td>
<td>Surface State</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolitic Graphite</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>NSCG</td>
<td>Natural Single-Crystal Graphite</td>
</tr>
<tr>
<td>FLG</td>
<td>Few-Layer Graphene</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>QHE</td>
<td>Quantum Hall Effect</td>
</tr>
<tr>
<td>QED</td>
<td>Quantum Electrodynamics</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
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**List of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>$E_B$</td>
<td>Electron binding energy (relative to the Fermi level)</td>
</tr>
<tr>
<td>$k$</td>
<td>Electron wave vector</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Electron emission angle (relative to the surface normal)</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Pass energy of the electron energy analyzer</td>
</tr>
<tr>
<td>$\Psi_i^N (\Psi_f^N)$</td>
<td>Wave function of the initial (final) state of the $N$-electron system</td>
</tr>
<tr>
<td>$\mathbf{A}$</td>
<td>Vector potential of the electromagnetic field</td>
</tr>
<tr>
<td>$\phi_i^k (\phi_f^k)$</td>
<td>Wave function of the initial (final) state of an electron with wave vector $k$</td>
</tr>
<tr>
<td>$F(E)$</td>
<td>Fermi-Dirac function</td>
</tr>
<tr>
<td>$\mathbf{A}(\mathbf{k}, \omega)$</td>
<td>Electron spectral function at wave vector $\mathbf{k}$ and energy $\omega$</td>
</tr>
<tr>
<td>$\mathbf{G}(\mathbf{k}, \omega)$</td>
<td>Green’s function of the electron</td>
</tr>
<tr>
<td>$\Sigma(\mathbf{k}, \omega)$</td>
<td>Complex electron self-energy</td>
</tr>
<tr>
<td>$r_i (r_s)$</td>
<td>Reflectivity of the electron wave at the interface (surface)</td>
</tr>
<tr>
<td>$\Phi_i (\Phi_s)$</td>
<td>Phase shift of the electron wave at the interface (surface)</td>
</tr>
<tr>
<td>$N$</td>
<td>Film thickness in unit of monolayer</td>
</tr>
<tr>
<td>$t$</td>
<td>Interlayer spacing</td>
</tr>
<tr>
<td>$\mathbf{g}$</td>
<td>Reciprocal lattice vector</td>
</tr>
<tr>
<td>$\mathbf{e}$</td>
<td>Unit polarization vector of the phonon</td>
</tr>
<tr>
<td>$\Sigma_{\text{e-ph}}(\omega, \mathbf{p} \mathbf{T})$</td>
<td>The electron-phonon part of the electron self-energy</td>
</tr>
<tr>
<td>$V(\mathbf{r})$</td>
<td>The rigid ion potential</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Charge spillage parameter</td>
</tr>
<tr>
<td>$M$</td>
<td>Matrix element of the interface potential</td>
</tr>
<tr>
<td>$b$</td>
<td>The terrace width of Si(557)-Au surface</td>
</tr>
<tr>
<td>$E_D$</td>
<td>The Dirac point energy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>The Fermi level</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Substrate Effects on Quantum Well States

Ultrathin metallic films grown on semiconductor substrates are ubiquitous components of solid-state devices. As the feature size of current electronic devices approaches the nano-scale, a fundamental understanding of the physical consequences of shrinking the devices is becoming increasingly important. When the thickness of a thin film becomes comparable to the electronic coherence length, quantum effects, including coherence and interference, can become dominant influences on physical properties. A well-known consequence of such effects is the formation of electronic standing waves, i.e., quantum well states (QWS) [1,2,3,4]. In its simplest form, QWS can be understood as a particle confined in a box. Conventionally, the substrate influence on the QWS is taken into account by a phase shift and reflectivity at the film-substrate interface [5]. This simple picture in terms of Fabry-Pérot modes is proven to be quite successful in explaining major experimental features of QWS observed by photoemission.

However, recent experiments reveal fine structures in the QWS that cannot be understood based on this standard QWS model. For example, in Ag films grown on Ge(111), a sharp “kink” in the QWS can be observed near the Ge band edge (see Fig. 4.2) [6]. This kink is a manifestation of the many-body interaction, which is caused by the coupling between the QWSs and the electrons in the substrate. Another work in Ag films grown on highly doped n-type Si(111) reveals fine-structured electronic fringes near the silicon valence band edge (Fig. 1.1). These fringes suggest that coherent electronic interference exists across the incommensurate interface. In other words, the electron wave functions in the film and substrate are matched at the interface plane and the resulting electronic state is coherent throughout the entire system. These studies show that the substrate does not simply act like a “mirror” that (partially) reflects electrons. Electronic coupling and coherence at the interface should be taken into account if a thorough understanding of the system is required.

The first experiment in this dissertation studies another important effect at the interface: diffraction (chapter 4). When the electron wave impinges upon the interface, it can undergo diffraction from the interface, whose periodicity differs from the film. This diffracted wave can interfere with the original electron wave and leads to electronic interference structures at the
Brillouin zone boundaries of the substrate [8]. Our work employs a prototypical metal-semiconductor system, i.e., Ag films on Ge(111). In order to systematically study these electronic interference structures, we mapped the electronic structures in \( k \) space and performed similar measurements at various film thicknesses. Cuts in the momentum space at constant energies near the Fermi surface reveal intricate patterns that resemble interfering waves emanating from multiple centers (Fig. 4.2). The measured dispersion relations exhibit zigzag patterns with multiple energy gaps. This complex band structure is well reproduced by our model calculation, which incorporates the mixing of electronic standing wave by the Ag-Ge interface potential. In addition, the interaction strength is found to be inversely proportional to the film thickness, as expected from the spatial confinement of the interface potential.

The second experiment examines the electronic structures of corrugated Ag and Pb films grown on the Si(557)-Au surface (chapter 5). This project is initially motivated by the possibility of creating quasi-1D electron system on a stepped Si(111) surface. Recent works on atomic wires grown on stepped Si(111) substrates indicate that some chain structures exhibit quasi 1D characters and they might be good templates for growing quasi 1D structures, e.g., stripes [9,10]. A central issue in our study is the dimensionality of the QWS in these corrugated films: are the QWSs free to propagate across the steps, thus forming Bloch-like waves? Or, are they confined by the steps to form localized states?

Our photoemission measurements in both Ag and Pb films show that the QWSs are 2D and quantized along the optical normal of the surface, i.e., the Si [557] direction. In addition, the electrons are coherent across the steps, leading to modified QWS dispersion compared to its counterpart in a flat film. Specifically, the QWSs in corrugated Ag and Pb films are centered at the Brillouin zone boundaries corresponding to the step modulation (Fig. 5.7). This indicates that the interference of QWS is affected by diffraction from the step superlattice. In a sense, the film becomes a one-dimensional cavity (along the \( z \) direction) bounded by two parallel gratings, and QWSs form in the cavity by two conjugate umklapp diffractions at the surface and interface. An important characteristic of these diffraction gratings is that they are strongly blazed. This means that only those diffraction orders that nearly satisfy the reflection geometry for each (111) facet are important. This blazed diffraction is essential for understanding the photoemission spectra at various photon energies.
Controlled modification of material structures at the nanoscale is a key concept underlying advanced applications and device designs. The two experiments above demonstrate that the electronic structures of ultrathin metal films can be modulated and tuned by the substrate. In particular, these modifications result in a change in the Fermi surface, which could in turn affect the transport properties of the films. The film thickness can be controlled at the atomic level by deposition. Stepped surfaces with different step periodicity can be prepared by varying the miscut angle. These degrees of freedom allow for the preparation of thin metallic films with tailored geometries suitable for applications.

1.2 Electron-Phonon Coupling in Graphite/Graphene

Graphene systems, made of sheets of carbon atomic layers, have linear band dispersion relation near the K point. In freestanding graphene, these linear bands (π bands) cross each other exactly at the Fermi level. This peculiar band structure indicates that the charge carriers in graphene are massless Dirac Fermions, which are described by the Dirac equation, instead of by the Schrödinger equation. A manifestation of the massless Dirac Fermions is the anomalous half-integer quantum hall effect (QHE), which was discovered in 2004 [11,12]. This discovery marks the beginning of the gold rush for graphene. Graphene systems are important for two primary reasons. First, due to their relativistic massless charge carriers, table-top condensed matter experiments can be performed to test fundamental problems in quantum electrodynamics (QED) [13]. Second, electron mobility in graphene is very high, and the charge carrier concentration can be easily tuned by an external electric effect. These electrical properties make graphene a promising material for next generation high-power, higher-frequency electronic devices.

The intrinsic resistivity of graphene is determined by electron-phonon (e-ph) scattering [14]. Therefore, a complete understanding of this fundamental interaction is crucial for graphene-based electronics. Electron-phonon coupling in graphene has been studied by both angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM). By measuring the phonon “kink” in the quasiparticle dispersion relation, the electron-phonon coupling in graphene has been studied extensively by photoemission [15,16]. These studies show that the electrons couple preferably with the in-plane phonons at the K point (~150 meV), although a weak coupling with the out-of-plane phonons at the K point has also been observed. A recent study by STM shows gaps in the $dI/dV$ curve of graphene (see Fig. 1.2) [17]. The
gaps are attributed to phonon-mediated inelastic tunneling, i.e., tunneling from the electrons at the Dirac cones via coupling of phonons at the K point. Phonons thus act as a “floodgate” that controls the flow of tunneling electrons in graphene. The dominant contribution to the gaps is from the out-of-plane phonons at the K point (~67 meV). However, there have been disagreements about the gap size or even the existence of gaps in previous STM studies \[18,19,20,21\]. The inconsistencies could be related to sample inhomogeneity, tip structure, or tunneling at the buried interface.

While previous photoemission studies of graphene have focused on the quasiparticle band dispersion relations, we take a different approach by measuring the spectral regions far away from the quasiparticle bands (chapter 6). Although direct emission from the quasiparticles is forbidden in this region, indirect emission through coupling to phonons is allowed. Our ARPES measurements of graphite and graphene layers reveal gaps at normal emission, one at ~67 meV and another much weaker one at ~150 meV (Fig. 6.9). These gaps are universal among various graphene systems, including single-crystal graphite and graphene layers with different coverages. They are independent of photon energy and temperature up to 300 K. After careful consideration of various possible scattering channels, we conclude that the gaps are caused by photoemission of electrons at the Dirac cones via coupling of a phonon at K point. Since the Debye temperature of graphite is much higher than the measurement temperature, phonon emission dominates the process.

Interestingly, our results bear strikingly similarities to the STM data. Since ARPES is free of tip effects, which are generally an issue with STM measurements, our study provides another convincing evidence of such electron-phonon scattering process in graphene systems. Another advantage of ARPES is its angular resolution, which allows us to probe the momentum dependence of the gaps. Experimentally, the gaps gradually disappear as the in-plane momentum increases, because phonons at lower wave vectors, and lower energies, become involved. In a sense, we established a connection between the normal emission spectrum in ARPES and the tunneling spectrum from STM for the case of graphene systems. The underlying mechanism for this link is the same electron-phonon scattering process. The combined results from ARPES and STM show that electron-phonon coupling controls the transmission and tunneling properties of graphene device and the dominant contribution comes from the coupling with out-of-plane phonons at the K point.
Another important conclusion from the current study is that ARPES spectral regions forbidden for direct emission provide a valuable test ground for detailed investigations of elementary interactions. This method should work well for systems with a simple Fermi surface, such as graphene systems. Possible future applications of this method include phonon spectroscopy and determination of the electron-phonon coupling strength through a detailed analysis of ARPES data.

1.3 Thesis Overview
This thesis is organized as follows: Chapter 2 provides an introduction to the method of angle-resolved photoemission spectroscopy, including some experimental details (Sec. 2.3 and 2.4) and a well-established theory for understanding photoemission (Sec. 2.5). Chapter 3 provides the necessary theoretical background for understanding the work in this dissertation. Two major topics are covered in this chapter, namely, quantum well states (Sec. 3.2) and electron-phonon coupling (Sec. 3.3). Chapter 4 describes our study of Ag films grown on Ge(111). Chapter 5 presents our work on Ag and Pb corrugated films grown on the Si(557)-Au surface. Chapter 6 describes our discovery of the phonon-induced gaps in graphene systems. Finally, some possible directions for future research are discussed in Chapter 7.

REFERENCES
Figure 1.1. Coherent electronic fringe structure in Ag films grown on n-type Si(111) substrates [7]. Photoemission data for 8 ML Ag film grown on (A) lightly doped n-type Si and (B) highly doped n-type Si. (C) is an enlarged view of the region contained within the rectangular box in (B). (D) is a plot of the QWS wave functions at $k_x$=0.22Å$^{-1}$ for 8 ML Ag film.
Figure 1.2. Phonon-induced gaps in the tunneling spectra of graphene, adapted from [17]. The $dI/dV$ spectra are taken at the same point on the graphene surface for different gate voltages, $V_g$. Changing the gate voltage shifts the Fermi level relative to the Dirac point. Red arrows indicate the gate-dependent positions of the adjacent conductance minimum, $V_D$, outside the gap feature.
2 Angle-Resolved Photoemission Spectroscopy

2.1 Overview
Angle-resolved photoemission spectroscopy (ARPES) can directly map the band structures of solid materials. This unique advantage, together with its applicability to various material systems, has made ARPES a technique that is widely used to study solid state materials. This chapter provides an introduction to ARPES that will allow readers to understand the work presented in this dissertation. A simple physical picture of the ARPES process, which is based on a three-step model, will be presented first in order to provide readers with an intuitive understanding of photoemission (Sec. 2.2). ARPES experiment preparation and apparatus will be discussed in detail in Sec. 2.3 and Sec. 2.4, respectively. A more rigorous interpretation of photoemission will be offered in Sec. 2.5.

2.2 A Simple View of Photoemission Process
Figure 2.1 shows the typical experimental geometry for an ARPES experiment. Monochromatic photons with energy $h\nu$ are incident on the sample. Electrons are ejected from the sample, as a result of photoelectric effect, and reach the detector, where both the kinetic energy and the emission angle of the electrons are recorded.

The photoemission process is usually described by a three-step model [1]. This is a purely phenomenological model, but it captures the essential physics of photoemission, and has been widely adopted in the photoemission community [2]. Within this approach, the photoemission process is subdivided into three independent and sequential steps (see Fig. 2.2):

1. Optical excitation of the electron in the bulk.
2. Travel of the excited electron to the surface.
3. Escape of the photoelectron into vacuum.

In step (1), an occupied electronic state (initial state) is excited into an unoccupied state (final state) through photon absorption. Because the photons impart very little momentum, the momentum of the electron is essentially unchanged. Step (2) can be described in terms of an effective mean free path which is proportional to the probability that the excited electron will reach the surface without scattering. The inelastic scatterings of electrons give rise to a
continuous background in the photoemission spectra which is usually ignored or subtracted. Once the electron reaches the surface (step (3)), it overcomes the work function of the material and eventually emits from the surface. Within this process, the momentum perpendicular to the surface is not conserved, and the electron is refracted in a similar manner to that of light at the interface between two materials. Nevertheless, the parallel component of the momentum is still conserved (analogous to Snell’s Law).

Energy conservation requires

\[ E_{\text{kin}} = h\nu - \Phi_{\text{wf}} - |E_B|, \]

where \( E_{\text{kin}} \) is the kinetic energy of the electron in vacuum, \( \Phi_{\text{wf}} \) is the work function of the material, and \( E_B \) is the binding energy of the electron (relative to the Fermi level). The conservation of the parallel momentum allows us to write

\[ k_{\|} = \sqrt{\frac{2m_e}{\hbar^2} E_{\text{kin}} \sin \theta}, \]

where \( k_{\|} \) is the parallel wave vector of the initial state, \( \theta \) is the polar emission angle (Fig. 2.1). \( E_{\text{kin}}, \Phi_{\text{wf}} \) and \( \theta \) can all be measured directly from the experiment. Therefore, the energy and in-plane wave vector of the electronic state before photoemission can be determined from Eqs. (2.1) and (2.2). The results from an ARPES measurement are generally expressed as a three-variable photocurrent function \( I(E_B, k_x, k_y) \). Tracing the peaks in the photocurrent function allows us to obtain the in-plane dispersion of the occupied band. A plot of photocurrent as a function of energy for a fixed \((k_x, k_y)\) is called the energy distribution curve (EDC), while the momentum distribution curve (MDC) refers to the photocurrent as a function of \( k_{\|} \) at a fixed energy \( E_B \).

The perpendicular momentum of the initial state, \( k_{\perp} \), cannot be determined from ARPES in a direct manner. Extracting \( k_{\perp} \) requires knowledge of the final state dispersion, which is generally complicated. This is the well-known “\( k_{\perp} \) problem” in photoemission. In practice, if the final state of the electron has a large energy relative to the vacuum level, the final state can be approximated by a free-electron model

\[ E_f = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m_e} - V_0, \]

(2.3)
where $V_0$ is called the inner potential of the material. It is essentially the zero-order term in the expansion of the crystal potential and is typically on the order of 10 eV for most materials. Normally, Photoemission data are taken at various photon energies, and $V_0$ is obtained by matching the experiment with the theory. A detailed discussion of the photon energy dependence will be given in Sec. 2.5.1. This $k_{\perp}$ problem is not an issue for 2D systems, because there is no dispersion along the $z$ direction. Most of the systems studied in this dissertation are in this category.

The three-step model is only a phenomenological model, because the division of the photoemission process into three steps is artificial and unrealistic. A more accurate theory of photoemission that involves the rigorous quantum-mechanical treatment will be presented in Sec. 2.5.

### 2.3 Preparation for ARPES Experiment

Photoemission spectroscopy is notable for its surface sensitivity, a characteristic that is both a strength and a weakness. It allows the technique to probe surface-related electronic states, but it also restricts the method to separating the surface component from the bulk contribution. Photons have no trouble penetrating crystal samples, but the short mean-free path of photoelectrons limits the probe depth (step (2) in the three-step model). Fig. 2.3 displays a plot of the experimental mean free path $\lambda$ of electrons as a function of the kinetic energy [4]. This shows that $\lambda$ is almost material independent. Due to the constraint from the photoemission cross section, as well as the momentum resolution, ARPES experiments for valence electrons are typically carried out with the kinetic energy of electrons in the range of 10-200 eV. This indicates that the useful photoemission intensity comes from the first few atomic layers of the material. The electrons from deeper layers form a continuous secondary electron background as a result of inelastic scatterings. The surface sensitivity of ARPES requires that the sample surface stays clean and free of contamination during the measurement.

#### 2.3.1 Ultrahigh Vacuum
In order to keep the sample free of contamination during the measurement, the chamber must be under ultrahigh vacuum (UHV). For a surface in contact with an ideal gas at pressure $P$ and temperature $T$, the molecular flux per unit surface area in unit time can be written as

$$F = \frac{P}{\sqrt{2\pi mk_B T}},$$

(2.4)

where $m$ and $k_B$ are the molecular mass and Boltzmann constant, respectively. At the pressure of $10^6$ Torr and room temperature, the surface will become completely covered by gas molecules in approximately 1 second, assuming that every gas molecule that hits the sample surface will stick. Therefore, keeping the sample free of contamination for several hours means that a pressure typically lower than $10^{-10}$ Torr is preferred.

A routine procedure for attaining UHV in our chamber is as follows: First, the chamber must be made leak-tight, particularly at the joints of flanges. Rotary and turbo pumps are used initially to provide the minimum vacuum (typically $<2 \times 10^{-5}$ Torr) required to start the ion pump. Once the ion pump takes over, the chamber can achieve a pressure of $\sim 10^{-8}$ Torr within a few hours. In order to obtain the pressure required for ARPES measurement, a “bakeout” of the chamber is carried out, during which the chamber is heated to 150ºC for about 30 hours (depending on the system). In this process, most of the gas molecules that are absorbed by the inner walls of the chamber are pumped out by the ion pump. After the bakeout, the titanium sublimation pump (TSP) is used periodically to provide additional pumping power in the chamber.

Attaining and preserving UHV condition in the chamber is a prerequisite for a successful ARPES experiment. This process might sound rather straightforward, but it can sometimes be painful and tedious. Common sources of bad vacuum include leaks at the joints of flanges, UHV incompatible materials inside the chamber, etc. UHV incompatible materials, which generally have a large vapor pressure and cannot be removed by the bakeout procedure, include, but are not limited to, a majority of organic compounds, normal glues, and lead solder. One should ensure that the material is UHV compatible before putting it into the vacuum chamber.

The pressure is not the only parameter for judging whether a vacuum system is good. Another important criterion for a good vacuum is that the gas molecules inside the chamber do not chemically react with the sample. For example, if there are some oil molecules with large mass in your chamber, the Si sample can easily become contaminated, even if the pressure
reading appears normal. As regards materials such as high-$T_c$ cuprates, which react appreciably with gas molecules, particularly oxygen, the standard for a good vacuum is therefore higher.

### 2.3.2 In-situ Sample Preparation

Even if one has a single-crystal sample, one cannot simply put it into the chamber and make ARPES measurement directly. The surface sensitivity of ARPES requires certain in-situ treatment of the sample before the actual ARPES measurement is performed. In the case of Si, or graphene layers on SiC, the treatment involves simply heating the sample up to a temperature in excess of 1000ºC, which removes all of the oxides and impurities on the sample and results in a good surface for taking ARPES measurements.

As regards Ge and other metal substrates that have lower melting points, a different procedure known as sputtering is employed for sample preparation. The cleaning of the sample surface is achieved by ionizing and accelerating argon gas molecules that are introduced into the vacuum chamber to bombard the sample surface. This process removes the contamination on the surface and exposes the clean regions inside. The sputtering is normally followed by a sequential annealing, which restores the surface structure as a result of the argon bombard. The typical argon pressure for sputtering is $2 \times 10^{-5}$ Torr. The accelerating voltage and emission current of the sputter gun filament is typically 1 kV and 25 mA, respectively.

The majority of works in this thesis involve the growth of ultrathin metal films on semiconductor substrates. This is achieved by molecular beam epitaxy (MBE). A schematic diagram of our MBE system is shown in Fig. 2.4. The thermally emitted electrons from the tungsten filaments are accelerated by a high voltage in order to heat up the crucible. The high purity materials that are contained in the crucible evaporate and condensate onto the sample. The main advantage of MBE is that its deposition rate is generally slow, which allows the films to grow epitaxially. The deposition rate is controlled by the total power supplied to the crucible, which is proportional to the product of the high voltage and the emission current associated with this high voltage. To achieve a constant evaporation rate, the emission current is held constant by adjusting the current of the tungsten filament through an external feedback circuit. The actual deposition rate is calibrated by a water-cooled crystal thickness monitor (XTM). XTM calibrates the deposition rate by measuring the change of the oscillation frequency of a quartz crystal as a result of its mass change from the deposition. The inaccuracy of XTM is typically within ~10%.
2.3.3 Sample Characterization

Before taking the APRES measurement, it is important to first ensure the surface quality. The most common technique for surface characterization is electron diffraction, including low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). We make use of a RHEED system in our chamber for sample characterization. RHEED is based on the reflection of electrons with high kinetic energy (10 keV in our RHEED system) at a glazing angle (about 3-4° with respect to the sample surface). The electrons are diffracted by the sample surface, after which they illuminate a fluorescent screen. The glazing incidence angle ensures that the penetration depth of the electrons is limited to the top layers. Fig. 2.5 shows a schematic diagram of the diffraction geometry in RHEED. Given that RHEED mostly probes the surface structure, the reciprocal lattice consists of rods that run along the z direction (reciprocal rods). Every spot on the RHEED screen corresponds to a crossing of a reciprocal rod with the Ewald sphere. As a result of this diffraction geometry, the RHEED pattern consists of Laue circles (Fig. 2.5). It is normally straightforward to deduce the surface structure from the RHEED pattern, given that the geometric parameters, e.g., incidence angle and sample-to-screen distance, can be accurately measured.

The surface quality can be verified from the RHEED pattern. A well-ordered surface usually gives rise to sharp, intense diffraction spots with a low background. By contrast, the RHEED pattern from a disordered surface contains fuzzy spots with an large background. In addition, RHEED is also sensitive to the surface roughness. For a smooth surface, the diffraction spots should move continuously as the sample is rotated along the z axis. However, in the case of a rough surface with large 3D facets, the positions of the diffraction spots generally do not move (only intensities vary) with the azimuthal rotation.

The surface sensitivity of RHEED allows for a detailed investigation of structural change near the surface. This change, called surface reconstruction, is driven by energy minimization of the surface to reduce the number of dangling bonds on the surface. The result of the surface reconstruction is a rearrangement of the surface atoms into a surface lattice with a larger unit cell, which is commensurate with the bulk-truncated surface lattice. A famous example of surface reconstruction is the Si(111) 7x7 reconstruction, which has a “dimmer-adatom-stacking fault” structure [7]. “7” means that both sides of the unit cell (real space) are seven times the
bulk value. Fig. 2.6 displays a RHEED pattern for this surface. The bulk spots, which arise from the diffraction from the bulk, are normally identified by their sharpness, compared to their neighboring surface spots. The surface reconstruction can be directly obtained by counting the number of Laue circles between the main ones and the number of surface spots between bulk spots along a Laue circle.

2.4 ARPES Apparatus

Two key components of ARPES experiments are the light source and the electron analyzer. In the past, the limitations of the intensity of light source and resolution of electron analyzer significantly restricted ARPES studies. Nowadays, the development of synchrotron radiation light source and the state-of-art electron analyzer allow for a high-resolution Fermi surface mapping in only a few hours.

2.4.1 Light Source

All of the ARPES experiments in this thesis were carried out at Synchrotron Radiation Center (SRC), UW-Madison. In comparison with other laboratory light sources that use the characteristic emission lines of specific elements, the synchrotron light source is superior in terms of its high intensity, high level of polarization, high collimation, wide tunability of photon energy, etc.

The synchrotron radiation is generated by magnetically bending the electrons that are held inside a storage ring (Fig. 2.7(a)). Classical electrodynamics states that charged particles that undergo acceleration will emit electromagnetic radiation. In the case of electrons traveling in a circular orbit with a speed much less than \( c \), the radiation exhibits the usual toroidal radiation pattern, with its zero along the acceleration direction and its maximum along the direction of motion (see Fig. 2.8(a)) [9]. When the electron speed approaches \( c \), this radiation pattern is greatly distorted by virtue of relativistic effects calculated from the Lorentz transformation (Fig. 2.8(b)). The radiation is now constrained to a narrow cone with an angular width of \( \theta = \sqrt{1 - \beta^2} \). The electron energy in the storage ring at SRC is 800 MeV or 1 GeV, which means that the outcoming photons are sharply distributed along the direction tangential to the circular path of the electrons. This strong forward distribution gives rise to the high brightness
and low emittance of the synchrotron light source. In addition, the radiation spectrum is very broad, which allows for a wide tunability of the energies of photons (Fig. 2.7(b)).

In order to enhance the output photon flux, many insertion devices, wigglers or undulators, are installed along the storage ring. The intention is to create alternating magnetic fields along the electron path and force the electrons to undergo oscillations and radiate more photons (Fig. 2.7(a)). The photons coming out from each insertion device will then go through focusing mirrors and grating chambers to reach the user’s chamber. A beamline in a synchrotron facility refers to the combination of the insertion device, mirrors, slits, monochromatic gratings, etc.

The layout of a typical plane grating monochromator (PGM) beamline is shown in Fig. 2.9. The focusing mirrors are used to focus the beam spot typically to <1 mm. The slits are generally chosen so that the energy resolution of incoming photons matches the energy resolution of the electron analyzer. The monochromatic photon is obtained by utilizing the diffraction from a single crystal, e.g., Si. Since the direction of incident and outgoing photons is fixed in the grating chamber, the desired photon energy is attained by rotating the crystal to a specific angle in order to meet the Laue condition for this photon. At the same crystal position, there will be multiple photon energies that also satisfy the Laue condition (higher-order photons). This problem becomes more severe when the desired photon energy is low. In such a case, it is common to use filters to eliminate higher-order contamination.

Each beamline has its own characteristic that is suitable for one specific type of study. For example, the U-NIM beamline at SRC has a high flux at low photon energies, which permits APRES measurements with excellent momentum resolution. The PGM beamline has a high flux for a wide range of photon energies, which makes it an excellent choice for general APRES studies. The newly installed Apple beamline allows for continuous variations in the polarization of the incoming photons, which is useful for studying the symmetry of electron wave function.

2.4.2 Electron Analyzer

Modern electron analyzers employ 2D detectors, which allow for the simultaneous acquisition of energy distribution curves (EDC) at a wide angular range. This feature has greatly enhanced the rate of data acquisition. In addition, good angular and energy resolution ensure that the data is of high quality. Before entering into a discussion of the modern electron analyzer, we will first explain how the hemisphere electron energy analyzer works.
Fig. 2.10 shows a schematic diagram of a hemisphere electron energy analyzer. The electrons from the sample are focused and retarded by the lens and enter the analyzer through the entrance aperture. Only electrons that have the right kinetic energy can go through the hemisphere analyzer and reach the exit aperture without colliding with the inner walls of the analyzer. The kinetic energy of the electron traveling on the central path \( R_0 = \frac{R_1 + R_2}{2} \) is given by

\[
E_p = \frac{eV}{R_2 - R_1}.
\]

This energy is called the pass energy of the analyzer, and it is determined by the radii of the hemispheres and the voltage applied between them. Electrons that have the same kinetic energy but a different entrance angle can still reach the exit aperture, although they undergo slight different trajectories (refocusing occurs for hemisphere sectors at an angle of 180º). The pass energy is normally fixed during an EDC scan (for a constant energy resolution). In order to scan different energies, a retarding voltage is applied at the lens to decelerate the electrons to the pass energy.

The energy resolution of a hemisphere analyzer is calculated as [11]

\[
\Delta E = E_p \left( \frac{x_1 + x_2}{2R_0} + \alpha^2 \right),
\]

where \( x_1 \) and \( x_2 \) are the radii of the entrance and exit apertures, \( \alpha \) is the maximum angular deviation of the electron trajectories at the entrance and is determined by the lens system. It is obvious from Eq. (2.6) that a large hemisphere is inherently favored because of a better resolution. In reality, the pass energy and the aperture sizes are set to achieve a good compromise between signal intensity and energy resolution.

The electron analyzer, shown in Fig. 2.10, can only measure the photoemission spectrum at one emission angle (EDC) per scan. This makes Fermi surface mapping a formidable job. The invention of the 2D electron analyzer greatly increased the rate of data acquisition and allows Fermi surface mapping to be done in a few hours. Fig. 2.11 displays a schematic diagram of this analyzer with 2D detectors. The apertures are replaced by slits, which permits electrons with a wide range of emission angles to enter the analyzer simultaneously. The original point detector is
now a 2D detector. The position where an electron hit the 2D detector is determined by the electron’s kinetic energy and emission angle. The exact conversion between the positions on the detector and the electron’s kinetic energy/emission angle is taken into account in the Scienta software. Note that the energy window on the 2D detector is quite small. Therefore, the retarding voltage still has to be scanned (swept mode) if a large energy range is needed.

The resulting data after one scan is a 2D matrix, with one axis being the electron’s kinetic energy and the other one being the emission angle along a certain direction (see Fig. 2.12). The angular range is ~10 degrees in our analyzer. In addition to the rapid data acquisition rate, another advantage of this new analyzer is that subtle features in the photoemission data can be directly “visualized,” even in the original data. For example (Fig. 2.12), one can clearly identify the “kinks” of the Ag quantum well states as they cross the Ge band edge. Nevertheless, one disadvantage of this 2D detector is the non-linearity in the relation between the counting rate and the measured intensity. Therefore, the photoemission data needs to be processed properly in order to ensure that no artifacts arise from data normalization.

### 2.5 Photoemission Theory

Section 2.2 presented a simple physical picture of the photoemission process that is based on three-step model. This section will provide a more rigorous interpretation of photoemission, following some previous reviews on this subject [2,12,13,14].

Photoemission involves photoexcitation of the $N$-electron ground state $\Psi_i^N$ into one of the possible final states $\Psi_f^N$. The transition probability can be approximated by Fermi’s golden rule:

$$w_{f,i} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu),$$

(2.7)

where $E_i^N$ and $E_f^N$ are the initial- and final-state energies of the $N$-particle system. The interaction with the photon is treated as a perturbation and is given by

$$H_{\text{int}} = -\frac{e}{2mc} (2\mathbf{A} \cdot \mathbf{p} - i\hbar \nabla \cdot \mathbf{A}),$$

(2.8)

where $\mathbf{p}$ is the electron momentum operator and $\mathbf{A}$ is the electromagnetic vector potential. The first term in (2.8), $\mathbf{A} \cdot \mathbf{p}$, is called the direct transition term and is normally the dominant contribution to the photoemission intensity. It preserves the crystal momentum of the electron.
during photoexcitation. The $\nabla \cdot \mathbf{A}$ term is usually ignored by an appropriate choice of gauge. However, at a surface, this term is not negligible and can even be comparable to the direct transition term $\mathbf{A} \cdot \mathbf{p}$ [15,16]. A detailed discussion of this surface transition term is given in Sec. 2.5.2.

The wave function of the initial state can be written in the form of a Slater determinant as

$$\Psi_{i}^{N} = C \phi_{i}^{k} \Psi_{i}^{N-1},$$

(2.9)

where $\phi_{i}^{k}$ is the wave function of the initial state with momentum $\mathbf{k}$ before photoexcitation, $\Psi_{i}^{N-1}$ is the wave function of the remaining ($N$-1) electrons. $C$ is the operator that antisymmetrizes the wave function properly. The wave function of the final state, within the sudden approximation (assuming the electron is instantaneously removed by photoexcitation), can be written as

$$\Psi_{f}^{N} = C \phi_{f}^{k} \Psi_{f}^{N-1},$$

(2.10)

where $\phi_{f}^{k}$ is the wave function of the electron state after photoexcitation, $\Psi_{f}^{N-1}$ is the final state wave function of the ($N$-1) electrons left behind.

Therefore, we can write the matrix element in Eq. (2.7) as

$$\left\langle \Psi_{f}^{N} | H_{\text{int}} | \Psi_{i}^{N} \right\rangle = M_{f,i}^{k} \left\langle \Psi_{f}^{N-1} | \Psi_{i}^{N-1} \right\rangle,$$

(2.11)

Where $\left\langle \phi_{f}^{k} | H_{\text{int}} | \phi_{i}^{k} \right\rangle \equiv M_{f,i}^{k}$ is the one-electron matrix element, and the second term is the ($N$-1)-electron overlap integral. The first step of evaluating the overlap integral is to assume that the remaining orbitals are the same in the final state as they were in the initial state (called frozen-orbital approximation), meaning that $\Psi_{f}^{N-1} = \Psi_{i}^{N-1}$. This renders the overlap integral unity, and the transition matrix element is just the one-electron matrix element. Under this assumption, the photoemission experiment probes only one electron state ($\phi_{i}^{k}$ to $\phi_{f}^{k}$), which does not interact with the remainder of the ($N$-1) electrons. The resulting photoemission spectrum will be given by a delta function at the electron energy $\epsilon_{k}$.

In reality, this simple picture breaks down because the ejection of an electron from $\phi_{i}^{k}$ to $\phi_{f}^{k}$ disturbs the remaining ($N$-1) electrons system. The remaining system will readjust itself in
such a way as to minimize its energy (relaxation). We now assume that the final state of \((N-1)\) electrons has many possible excited states (labeled \(s\)) with wave functions \(\Psi_{s}^{N-1}\) and energies \(E_{s}^{N-1}\). Therefore, the total photoemission intensity measured as a function of electron kinetic energy at a momentum \(k\), namely, \(I(k;E_{\text{kin}}) = \sum_{fj} w_{fj}\), is then proportional to

\[
I(k;E_{\text{kin}}) = \sum_{fj} \left| M_{fj}^{k} \right|^{2} \sum_{s} \left| c_{s} \right|^{2} \delta(E_{\text{kin}} + E_{s}^{N-1} - E_{i}^{N} - \hbar\nu), \tag{2.12}
\]

where \(\left| c_{s} \right|^{2} = \left| \left\langle \Psi_{s}^{N-1} \right| \Psi_{i}^{N-1} \right|^{2}\) is the probability that the removal of an electron from the initial state \(k\) from the \(N\) electron ground state leaves the \((N-1)\)-electron system into the excited state \(s\). For strongly correlated systems, many of the \(c_{s}\) will be nonzero because the removal of the photoelectron results in a strong change of the system’s effective potential and, in turn, \(\Psi_{i}^{N-1}\) will overlap with many of the eigenstates \(\Psi_{i}^{N-1}\). Thus, the ARPES spectrum will not be a single delta function, but will instead show a main line and several satellites according to the number of excited states \(s\) created in the process.

The term \(\sum_{s} \left| c_{s} \right|^{2} \delta(E_{\text{kin}} + E_{s}^{N-1} - E_{i}^{N} - \hbar\nu)\) in Eq. (2.12) is essentially the spectral function of the electron. To see it, the wave function \(\Psi_{i}^{N-1}\) can be expressed as \(\Psi_{i}^{N-1} = c_{k} \Psi_{i}^{N}\), where \(c_{k}\) is the annihilation operator for an electron with wave vector \(k\). This term can be rewritten as

\[
\sum_{s} \left| \left\langle \Psi_{s}^{N-1} \right| c_{k} \left| \Psi_{i}^{N} \right\rangle \right|^{2} \delta((\hbar\nu - E_{\text{kin}}) - E_{s}^{N-1} + E_{i}^{N}). \tag{2.13}
\]

This is exactly the spectral function of an electron with wave vector \(k\) and energy \(\hbar\nu - E_{\text{kin}}\). The spectral function describes the probability of removing an electron (for \(E<E_{F}\)) or adding an electron (for \(E>E_{F}\)) with energy \(E\) and wave vector \(k\) from (to) the (interacting) \(N\) electron system. For a 2D single-band system, one can write the intensity measured in an ARPES experiment as

\[
I(k;\omega) = I_{0}(k;\nu,A)f(\omega)A(k;\omega), \tag{2.14}
\]

20
Where $k = k_\omega$ is the in-plane electron momentum, $\omega$ is the electron energy with respect to the Fermi level, and $I^0_0(k, \nu, A)$ is proportional to the squared one-electron matrix element $|M^k_{f,i}|^2$, which depends on electron momentum $k$, as well as the energy $\nu$ and polarization $A$ of the incoming photon. $f(\omega)$ is the Fermi-Dirac function, which accounts for the fact that photoemission probes only the occupied electronic states. $A(k, \omega)$ is the spectral function (not to be confused with the vector potential $A$ of the incoming photon).

Eq. (2.14) shows that the photoemission intensity is essentially the product of the squared matrix element $I^0_0(k, \nu, A)$ and the spectral function of the electron. For many 2D systems, $I^0_0(k, \nu, A)$ is a slowly varying function of electron momentum and energy, and therefore can be viewed as a constant within a small momentum and energy space. In these cases, photoemission directly probes the spectral function.

The spectral function is a key for understanding many-body physics. The spectral function is directly related to the Green’s function by

$$A(k, \omega) = \frac{\text{Im}\{G(k, \omega)\}}{\pi}. \quad (2.15)$$

In a correlated electron system, the Green’s function is described in terms of the electron self-energy $\Sigma(k, \omega)$. The real and imaginary parts of the self-energy contain all the information on the energy renormalization and lifetime, respectively, of an electron with band energy $\varepsilon_k$ and momentum $k$. The Green’s function can be written as

$$G(k, \omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(k, \omega)}. \quad (2.16)$$

The corresponding spectral function is

$$A(k, \omega) = -\frac{1}{\pi} \frac{\text{Im}\Sigma(k, \omega)}{[\omega - \varepsilon_k - \text{Re}\Sigma(k, \omega)]^2 + [\text{Im}\Sigma(k, \omega)]^2}. \quad (2.17)$$

Note that $\varepsilon_k$ is the bare band energy of the electron, assuming there is no electron-electron correlation. It is obvious from Eq. (2.17) that the resulting spectral function is a Lorentzian function.
When there is no interaction between the electrons, i.e., $\Sigma(k, \omega) = 0$, the spectral function is a delta function at $\varepsilon_k$. If the electron-electron correlation is adiabatically switched on, the system remains at equilibrium. However, any electron added into a Bloch state has a certain probability of being scattered out of it by a collision with another electron, leaving the system in an excited state in which additional electron-hole pairs have been created. The result of this electron-electron correlation is that the energy and lifetime of the electrons are changed. The slightly modified electron (with normalized mass), described by Eq. (2.17), is generally called a quasiparticle. One can view this quasiparticle as an electron dressed by virtual excitations that move coherently with the electron through the crystal. In a correlated electron system, the spectral function is a Lorentzian function, with its center and width determined by the energy and lifetime of the quasiparticle, respectively.

To summarize, photoemission, which directly probes the spectral function of the electron, can be used to study the quasiparticle dynamics in correlated electron systems. The peak positions and linewidths are directly linked to the electron-electron correlation, i.e., the electron self-energy, which makes ARPES a powerful tool for studying many-body physics. We should mention that these studies are generally carried out for 2D electron systems, where the spectral function primarily determines the spectrum features. For 3D electron systems, the one-electron matrix element could play the dominant role instead.

For some works in this dissertation, e.g., Chapter 5, we will compare ARPES data taken at different photon energies to gain some information about dispersion along the z direction. We will argue that the surface transition term is dominant for graphite/graphene (Chapter 6). These specific issues of photoemission will be discussed in the following two subsections.

### 2.5.1 Photon Energy Dependence

Photoemission spectra measured at various photon energies probe different $k$ s. The reason is as follows: the energy conservation (Eq. (2.7)) requires that the photoexcited electron gains the energy of the incoming photon, $\hbar \nu$. The dipole transition term in (2.8), $A \cdot p$, preserves the crystal momentum of the electron during photoexcitation [14]. Therefore, the photoexcitation caused by the dipole transition term is a direct optical transition [17]. In the case of a three-
dimensional crystal, the direct transition can only occur at a specific \( k_\perp \) for a given photon energy (See Fig. 2.13). As the photon energy is swept, different \( k_\perp \) is probed accordingly.

In order to investigate the dispersion along the \( z \) direction, photoemission spectra must be taken at various photon energies. Generally, spectra taken at different photon energies are converted to \( k \) space for a fair comparison. If the quasiparticle peak positions do not move when the photon energy is varied, there is no electronic dispersion along the \( z \) direction.

### 2.5.2 Surface Transition

Sec. 2.5 mentions that the \( \nabla \cdot A \) term is not necessarily small, especially near the surface. The dielectric discontinuity near the surface gives rise to a corresponding discontinuity in \( A_\perp \), which, upon differentiation, yields a delta function at the surface [16]. As a result, the matrix element between any initial and final state \( \left\langle \phi^k_i | \nabla \cdot A | \phi^k_f \right\rangle \) is nonzero provided that both states have a non-zero amplitude at the surface. The contribution from this surface term to the transition matrix element is proportional to the amplitudes of the wave functions at the surface, namely, of the form \( C \phi_i^k *(z0) \phi_f^k(z0) \), where \( z0 \) denotes the surface position. The coefficient \( C \) is approximately proportional to the dielectric constant of the material \( \varepsilon \) and the perpendicular component of the vector potential \( A_\perp \). The resulting spectral contribution from this surface term generally resembles the one-dimensional joint density of states.

Surface transition has been observed in many systems, e.g., in Ag(111) normal emission spectrum (Fig. 2.14). The direct transition peak from the Ag \( sp \) bulk band exhibits a pronounced asymmetry, with a long tail at higher energy. This asymmetry arises from the spectral contribution of the surface transition term, which resembles the density of valence states. In general, the dipole transition term dominates the photoemission spectrum when direct transition can be satisfied and surface transition gives rise to a small change to the lineshape. However, when the direct transition is forbidden, e.g., normal emission near the Fermi level for graphite and graphite (chapter 6), surface transition is expected to play the dominant role.

### REFERENCES


[8] Obtained from the official website of SRC.


[10] Obtained from the official website of Swiss Light Source (SLS).


FIGURES

Figure 2.1. A schematic showing the angle-resolved photoemission geometry. $hv$ is the incoming photon energy, and $\theta$ is the polar emission angle.

Figure 2.2. Understanding the photoemission process based on the three-step model [3].
Figure 2.3. Universal curve of the mean free path for the inelastic scattering of electrons in a solid [4].

Figure 2.4. A schematic diagram of our MBE system [5].
Figure 2.5. A schematic view of the diffraction geometry of RHEED [6]. The diffraction spots on the RHEED screen arise from crossings of the reciprocal rods (of the sample surface) with the Ewald sphere. The resulting RHEED pattern consists of Laue circles. Red (blue) lines correspond to Laue circle #0 (#1), respectively.

Figure 2.6. RHEED pattern of a Si(111)-7x7 reconstruction. The incident beam is along the $\bar{\Gamma}\bar{M}'$ direction ($[\bar{1} \bar{1} 2]$).
Figure 2.7. (a) A schematic diagram of light generation in a synchrotron radiation facility. (b) Synchrotron radiation spectrum of SRC [8].
Figure 2.8. Qualitative radiation patterns to be expected from electrons in a circular orbit (a) at low energy and (b) at high energy, adapted from [9].

Figure 2.9. Layout of the adress beamline (plane grating monochromator) at Swiss Light Source [10].
Figure 2.10. Schematic of a hemisphere electron energy analyzer.

Figure 2.11. Schematic of the Scienta electron analyzer with 2D detector (Energy and emission angle).
Figure 2.12. Original photoemission data shown as an image plot. The spectrum was taken from a 13 ML Ag film on Ge(111), measured along the $\Gamma M'$ direction ($[\overline{1}12]$ direction).

Figure 2.13. Probing different $k_\perp$ by varying the photon energy. The Figure uses the Ag $sp$ bulk band as an example [16]. Direct transitions for photon energies at 7, 8, and 9 eV are indicated by vertical arrows.
Figure 2.14. Surface transition in Ag(111) [16]. Top: a model fit (curve) to the normal emission spectrum (circles) of Ag(111), taking into consideration both the dipole (bulk) transition and surface transition. Middle: spectral contribution from the dipole transition term. Bottom: the density of valence states.
3 Theoretical Backgrounds

3.1 Introduction

This dissertation examines quantum well states (QWS) in ultrathin metallic films and electron-phonon (e-ph) coupling in graphite/graphene layers. The current chapter provides the necessary theoretical background for understanding these studies. Sec. 3.2 is intended to provide an introduction to QWS in thin films, based on its analogy to Fabry-Pérot interferometer. Conventionally, the substrate effect is taken into account by using a phase shift and reflectivity at the interface (Sec. 3.2). Sec. 3.3 will present an introduction to e-ph coupling and how it can be measured by ARPES.

3.2 Quantum Well States

If the thickness of a metallic film is comparable to the coherence length of the electron, the electronic states will differ dramatically from their bulk counterparts. Due to the electronic coherence and interference, the electrons can bounce back and forth between the two boundaries of the film and form electronic standing waves, known as quantum well states (QWS). The resulting electronic states are quantized along the z direction, i.e., the allowed momenta along the z direction are discrete and depend on the film thickness and boundary conditions (Fig. 3.1).

Calculating the QWSs in a rigorous manner requires solving the Schrödinger equation for the whole film-substrate system. This is generally difficult to tackle, especially when there is strong electronic interaction between the film and substrate. An easy way to interpret the QWS is to invoke the analogy between the QWS and the Fabry-Pérot interferometer [1]. In fact, this simple picture of QWS has proven to be rather successful for explaining many QWS phenomena.

QWS is formed by multiple reflections between the two confining boundaries (Fig. 3.2). Therefore, electron waves become modulated by an interference factor

$$\frac{1}{1 - r_s r_i \exp[i(2\pi N t + \Phi_s + \Phi_i)] \exp(-Nt/\lambda)},$$

where $r_s$ and $r_i$ are the reflectivities at the surface and the interface, $k$ is the electron wave vector, $N$ is the film thickness in monolayers, $t$ is the monolayer thickness, $\Phi_s$ and $\Phi_i$ are the phase shifts at the surface and interface, and $\lambda$ is the quasiparticle mean free path. The photoemission
transition matrix element, relative to the bulk case, is modulated by the interference factor in Eq. (3.1). The photoemission intensity is in turn modulated by the absolute square of the same factor. Thus, the photoemission spectrum for a quantum well becomes

\[ I \propto \frac{C(E)}{1 + \left( \frac{4f^2}{\pi^2} \right) \sin^2(k\Delta t + \Phi_s + \Phi_i)}, \quad (3.2) \]

where \( C(E) \) is the squared bulk matrix element at energy \( E \). The quantity \( f \) is the Fabry-Pérot finesse (ratio of peak separation to peak width) given by [2]

\[ f = \pi \sqrt{r_{ss} \exp(-Nt / 2\lambda)} \frac{1 - r_{ss} \exp(-Nt / \lambda)}{1 - r_{ss} \exp(-Nt / \lambda)}. \quad (3.3) \]

Eq. (3.2) yields a set of peaks at positions where the sine function in the denominator equals zero; the resulting condition is just the famous Bohr-Sommerfeld quantization rule

\[ 2k(E)Nt + \Phi_i(E) + \Phi_s(E) = 2n\pi. \quad (3.4) \]

The quantization condition states that the accumulated phase shift after a round trip should be an integer of \( 2\pi \). The peak width \( \delta E \) is

\[ \delta E = \hbar \eta \frac{1 - r_{ss} \exp(-1/ \eta)}{\sqrt{r_{ss} \exp(-1/ (2\eta))}}, \quad (3.5) \]

where \( \Gamma \) is the quasiparticle inverse lifetime and is related to the group velocity \( v \) by \( \Gamma = v/\lambda \), and \( \eta = \lambda/(Nt) \). The quantities \( k \) and \( \Gamma \) (related to the real and imaginary parts of the electron self-energy) and \( r \) and \( \Phi \) (related to the confinement potential) are of basic interest and completely specify the interferometer properties. While \( k \) and \( \Phi \) determine the peak positions through Eq. (3.4), \( \Gamma \) and \( r \) control the peak width through Eq. (3.5). They all depend on the electron energy \( E \), but not on the film thickness \( N \).

In general, the electron wave vector \( k \) and group velocity \( v \) as a function of energy are derived from the bulk band structure. The reflectivity at the surface, \( r_s \), should be unity. The reflectivity at the interface, \( r_i \), depends on the interface potential and the electron energy. The phase shifts, \( \Phi_i \) and \( \Phi_s \), are related to the logarithmic derivatives of the wave functions at the boundaries. The electron mean free path is normally much larger than the film thickness (for sp electrons). Therefore, Eq. (3.5) can be simplified as
\[ \delta E = \frac{\hbar v}{Nt} \frac{1-r_i}{\sqrt{r_i}}. \]  

(3.6)

When \( r_i \) is less than 1, the QWS is also called quantum well resonance. The wave function of quantum well resonance penetrates into the substrate and forms a resonant state.

According to Eq. (3.4), when the Fermi wave vector \( k_F \) is not at the zone boundary, the QWS periodically crosses the Fermi level as the film thickness \( N \) varies. The periodicity is simply

\[ \Delta N = \pi / (k_F t). \]  

(3.7)

This periodic crossing of QWS at the Fermi level results in an oscillation of the density of states (DOS) at the Fermi level as a function of \( N \). Because the DOS at the Fermi level is directly related to many physical properties such as resistivity, superconducting transition temperature, thermal stability, etc., these physical properties are expected to exhibit oscillations with the film thickness [3].

The substrate modifies the QWS energy positions and the peak widths, through the reflectivity and phase shift at the interface (Eqs. (3.4) and (3.5)). The following two subsections will discuss these two quantities in the cases of two prototypical interfaces (Sec. 3.2.1 and 3.2.2). The comparison between QWS and the surface state (SS) will be given in Sec. 3.2.3.

3.2.1 QWS in Freestanding Films

Freestanding films essentially have no interaction with the substrate. At the interface, the reflectivity is unity and the phase shift is close to that at the surface. Due to this simplicity, the band structure for a freestanding film can be rigorously calculated. In reality, interaction between the film and substrate always exists, though it may be quite weak. The translational symmetry of the film is broken due to the substrate, and the band structure becomes difficult to calculate directly. However, by choosing a particular substrate that has minimal interaction with the film, quasi-freestanding film can be grown.

One example of quasi-freestanding films is Pb(111) film grown on highly oriented pyrolitic graphite (HOPG) [4]. The normal emission spectra show multiple sharp QWS peaks at various nominal Pb coverages (Fig. 3.3(a)). This indicates that the film growth mode is three dimensional involving simultaneously several thicknesses centered about the nominal film
coverage. A detailed analysis of the spectra allows us to identify each QWS peak and its corresponding film thickness (Fig. 3.3(b)). The phase shift at the interface is found to be quite close to that at the surface (Fig. 3.3(c)), which suggests that the Pb-graphite interface is not very different from a Pb-vacuum interface. The phase shift at the Pb-vacuum interface is obtained from a first-principle calculation [5]. The intensities of prominent QWS peaks are plotted in Fig. 3.4(a) as a function of the nominal film coverage. The peaks corresponding to even- \( N \) thicknesses are much more intense than the odd- \( N \) thicknesses, indicating that the system favors the formation of even- \( N \) thicknesses. This can be understood in terms of Fig. 3.4(b), which displays the surface energies for different thicknesses of freestanding Pb films. The calculated surface energies for odd \( N \) are generally higher than those for nearby even \( N \), which suggests a bilayer oscillation. This bilayer oscillation is caused by the Fermi wave vector \( k_F \) of Pb along the [111] direction, which leads to \( \Delta N = 2.2 \) ML (Eq. (3.7)), i.e., a bilayer oscillation. Furthermore, the surface energies for \( N=1 \) and 3 are much higher than the rest, thus accounting for the absence of QWS peaks corresponding to \( N=1 \) and 3. At higher thicknesses, the even-odd selection becomes less pronounced due to the damping of the quantum oscillations in surface energy. Therefore, the observed spectra are well explained by the calculations of freestanding Pb(111) films.

In general, it is difficult to grow uniform freestanding films due to the weak interaction between the film and substrate. The weak interaction leads to little kinetic constraint of the atoms, and, therefore, 3-D island growth is more favorable [6]. The height distribution of these 3-D islands is caused by the interplay between the total energy minimization and the thermal fluctuation.

### 3.2.2 QWS in Metallic Films on Semiconductor Substrates

Thin metallic films grown on semiconductor substrates are particularly important due to their technological importance. The phase shift and reflectivity of QWS at the metal-semiconductor interfaces exhibit universal characteristics [7]. First, the reflectivity must be unity within the semiconductor band gap, i.e., \( r_i = 1 \) for \( E > E_0 \). Here \( E_0 \) is the energy of the semiconductor valence-band edge. The reason for this is obvious: the wave functions of electrons within the semiconductor band gap cannot penetrate into the substrate, which results in a total reflection of
the electron wave. Second, the phase shift should be close to a constant below the band edge, i.e., \( \Phi_i(E) = \Phi_0 \) for \( E < E_0 \), based on Huygens-Fresnel principle [8].

Near the semiconductor band edge, the phase shift and reflectivity of the electrons are analytically related. More specifically, the complex reflection coefficient at the interface, \( r_i \exp(i\Phi_i) \), must be an analytic function of electron wave vector \( k \). The analyticity of \( r_i \exp(i\Phi_i) \) permits the expansion in terms of \( k \), and the expansion coefficients at \( E_0 \) should be the same below and above the band edge. A straightforward derivation yields the following relations

\[
\Phi_i = \Phi_0 + a \sqrt{E - E_0} \Theta(E - E_0), 
\]

\[
r_i = 1 - \left[ a \sqrt{E_0 - E} - \frac{a^2}{2}(E_0 - E) \right] \Theta(E_0 - E),
\]

where \( \Theta \) denotes the unit step function, and \( a \) is a constant that is related to the direct gap of the semiconductor at the Brillouin-zone center. Eq. (3.8) and (3.9) show that both \( r_i \) and \( \Phi_i \) has a \( \sqrt{E} \) van Hove-type singularity with the same coefficient but opposite signs. These conjugate singularities, which occur on different sides of \( E_0 \), are a direct result of the kinematic constraints of electron reflection near the band edge. This relation between the phase shift and reflectivity is confirmed by our experiment in Pb-Si(111) interface (Fig. 3.5). The phase shift and reflectivity of Pb valence electrons across the Si valence-band edge can be determined experimentally by measuring the QWS positions and widths (Eq. (3.4) and (3.6)). Using submonolayer amounts of Au as an interfactant allows for a systematic adjustment of the band edge \( E_0 \). Both the phase shift and reflectivity near the Si band edge are almost interfactant-independent after correcting the \( E_0 \) offset, and the conjugate singularities between these two quantities can be clearly observed.

### 3.2.3 QWS vs Surface State

We mention surface state (SS) frequently in this dissertation. Surface state (SS) is an evanescent wave associated with a terminated crystal surface. Electrons at a truncated surface experience a different potential in comparison with the periodic potential of the bulk. This modified potential could give rise to new electronic states that are localized near the surface exclusively.
One way of looking at the SS is to regard it as an electron trapped between the surface of the crystal (via a bandgap) and the surface barrier potential, which prevents them from escaping into the vacuum (Fig. 3.6) [9]. If we use \( r_c \exp(i\phi_c) \) and \( r_b \exp(i\phi_b) \) to denote the respective complex reflection coefficients, the existence of a surface state requires

\[
  r_B = r_C = 1 \quad \text{and} \quad \phi_B + \phi_C = 2n\pi ,
\]

where \( n \) is an integer. This is a Bohr-like quantization condition on the round-trip phase accumulation, similar to the quantization condition for QWS (Eq. (3.4)). The electron energy of SS should be lower than the vacuum energy \((r_B=1)\) and also be within the band gap of the crystal \((r_C=1)\).

The phase shifts, \( \phi_B \) and \( \phi_C \), can be obtained by matching the wave functions at two boundaries [10,11]. Once \( \phi_B \) and \( \phi_C \) are known, the energy of the surface state can be deduced directly from the quantization condition (Eq. (3.10)). The SS wave function decays exponentially from the surface into the vacuum. Inside the crystal, the wave function of SS is a rapidly damped oscillating function. Within the nearly-free-electron two-band model, the wave vector of the SS electron within the crystal is a complex number, i.e.,

\[
  k_z = g_z / 2 + iq ,
\]

where \( g_z \) is the reciprocal lattice vector along the \( z \) direction, and \( q \) is related to the damping of the SS wave function into the bulk crystal.

A large part of this dissertation deals with the Ag(111) surface (chapter 4 and 5), which has a surface state very close to the Fermi level. This surface state is called Shockley surface state [12] and is the solution to Eq. (3.10) with \( n=0 \). The states with \( n=1,2,\ldots \) are called image potential states, and they have their wave function amplitude centered close to the surface barrier potential. These states are above the Fermi level and can only be observed by inverse photoemission.

Finally, let us summarize the characteristics of the wave functions for surface state, quantum well state and quantum well resonance (Fig. 3.7). SS is an evanescent wave associated with the crystal surface and is spatially confined near the surface. QWS are standing waves confined by two boundaries and are derived from bulk states. QW resonance is similar to QWS, except that its wave function penetrates deep into the substrate.
3.3 Electron-Phonon Coupling

Electron-phonon (e-ph) coupling is an important subject in solid state physics. It can be intuitively understood as processes in which an electron absorbs or emits a phonon (or phonons), changes its energy (wave vector) by the phonon energy (wave vector) and scatters into another electron state. The result from this coupling is the modified band dispersion and lifetime of the quasiparticle (polaron). The intrinsic resistivity of metals is mostly due to e-ph scatterings. In addition, e-ph coupling plays a key role in many exotic physics phenomena, including superconductivity, charge density waves, and structure phase transitions. This section is intended to give a brief introduction to this subject. Readers with a particular interest in this topic are referred to the book by G. Grimvall [13].

3.3.1 Electron-Phonon Scattering Matrix Element

Almost all calculations of the e-ph interaction in metals rely on the rigid-ion approximation. This assumes that the potential from the ion rigidly follows its motion. We will adopt this approximation in the current discussion.

Consider $N$ like ions, with electron cores which can be regarded as being tightly bound to the nuclei. The positions of the ions are $\mathbf{R}_j = \mathbf{R}^0_j + \mathbf{u}_j$, where $\mathbf{R}^0_j$ is the primitive lattice vector and $\mathbf{u}_j$ is the deviation from the equilibrium position due to thermal vibration (phonon). Each ion has $Z$ conduction electrons with coordinates $\mathbf{r}_i$ ($i=1, \ldots, ZN$). The total Hamiltonian for electrons and ions is

$$
\mathbf{H}_{\text{tot}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{ZN} \nabla^2 \mathbf{r}_i - \frac{\hbar^2}{2M} \sum_{j=1}^{N} \nabla^2 \mathbf{R}_j + \frac{1}{2} \sum_{i,k=1}^{ZN} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_k|} 
+ U_{\text{ion-ion}}(\mathbf{R}_1', \ldots, \mathbf{R}_N') + U_{\text{ion-electron}}(\mathbf{r}_1', \ldots, \mathbf{r}_{ZN}; \mathbf{R}_1', \ldots, \mathbf{R}_N').
$$

(3.12)

The first two terms are kinetic energies for electrons and ions. The last three terms are the potential energies for electron-electron interaction, ion-ion interaction and ion-electron interaction, respectively. It is assumed that the total wave function $\Psi_{\text{tot}}$ for conduction electrons and ions is the product of the two wave functions, $\Psi_e$ for electrons and $\Psi_{\text{ion}}$ for ions;

$$
\Psi_{\text{tot}} = \Psi_e \Psi_{\text{ion}}.
$$

(3.13)
\( \Psi_{\text{ion}} \) is a function only of the coordinates of ions and of the time \( t \);

\[
\Psi_{\text{ion}, \beta} = \Psi_{\text{ion}, \beta}(\mathbf{R}_1, \ldots, \mathbf{R}_N; t).
\] (3.14)

\( \Psi_{\text{e}} \) depends not only on the coordinates of the electrons, but also parametrically on the positions of ions;

\[
\Psi_{\text{e}, \alpha} = \Psi_{\text{e}, \alpha}(\mathbf{r}_1, \ldots, \mathbf{r}_{ZN}; \mathbf{R}_1, \ldots, \mathbf{R}_N; t).
\] (3.15)

Here \( \alpha \) and \( \beta \) are quantum numbers that specify the quantum states completely.

We first consider the part of the total Hamiltonian which contains electron coordinates,

\[
\hat{H}_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{ZN} \nabla^2_{\mathbf{r}_i} + \frac{1}{2} \sum_{i<k}^{ZN} \frac{\mathbf{e}^2}{|\mathbf{r}_i - \mathbf{r}_k|} + U_{\text{ion-electron}}(\mathbf{r}_1, \ldots, \mathbf{r}_{ZN}; \mathbf{R}_1, \ldots, \mathbf{R}_N).
\] (3.16)

For a certain configuration of ions (\( \mathbf{R}_1, \ldots, \mathbf{R}_N \)), we assume that we can find the solutions \( \Psi_{\text{e}, \alpha} \) to the equation

\[
\hat{H}_e \Psi_{\text{e}, \alpha} = E_\alpha \Psi_{\text{e}, \alpha},
\] (3.17)

where \( E_\alpha \) is a function of the coordinates of the ions, i.e., \( E_\alpha = E_\alpha(\mathbf{R}_1, \ldots, \mathbf{R}_N) \). Now we insert Eq. (3.13) into the complete Schrödinger equation

\[
\hat{H}_{\text{tot}} \Psi_{\text{tot}} = E_{\text{tot}} \Psi_{\text{tot}}.
\] (3.18)

When Eq. (3.18) is multiplied from the left by \( \Psi_{\text{e}, \alpha}^* \) and integrated over all the electron coordinates \( \mathbf{r}_i \) (\( d^3 \mathbf{r}_1 \ldots d^3 \mathbf{r}_{ZN} = d\mathbf{r}_e \)), the result is

\[
\sum_{j=1}^{N} \left[ -\frac{\hbar^2}{2M} \nabla^2_{\mathbf{R}_j} + U_{\text{ion-ion}} + E_\alpha \Psi_{\text{ion,} \beta} + (\Delta H) \Psi_{\text{ion,} \beta} \right] = E_{\text{tot}} \Psi_{\text{ion,} \beta},
\] (3.19)

where

\[
(\Delta H) \Psi_{\text{ion,} \beta} = -\frac{\hbar^2}{2M} \sum_{j=1}^{N} \left( \int \Psi_{\text{e}, \alpha}^* \nabla^2_{\mathbf{R}_j} \Psi_{\text{e}, \alpha} d\mathbf{r}_e \right) \Psi_{\text{ion,} \beta} - 2 \frac{\hbar^2}{2M} \sum_{j=1}^{N} \left( \int \Psi_{\text{e}, \alpha}^* \nabla_{\mathbf{R}_j} \Psi_{\text{e}, \alpha} d\mathbf{r}_e \right) \nabla_{\mathbf{R}_j} \Psi_{\text{ion,} \beta}.
\] (3.20)

The term \( (\Delta H) \Psi_{\text{ion,} \beta} \) is generally small. If we simply neglect it, Eq. (3.19) is a Schrödinger equation for the ions in which the energy eigenvalues \( E_\alpha \) of the electrons act as an effective
potential for the movement of ions (screening). Hence, we have achieved the goal of separating the Schrödinger equation of ions from that of electrons.

Now let us consider the matrix element of the total Hamiltonian

$$\langle \alpha', \beta' | H_{\text{total}} | \alpha, \beta \rangle.$$  \hspace{1cm} (3.21)

where the wave functions $| \alpha, \beta \rangle$ are the products of separate electronic and phonon parts in accordance with the adiabatic approximation. If we neglect the term $(\Delta H)$ defined in Eq. (3.20), the matrix element is zero unless $\alpha=\alpha'$ and $\beta=\beta'$. Thus, the contribution to the non-diagonal matrix element is entirely from the $(\Delta H)$ term. The non-diagonal matrix element with $(\Delta H)$ kept is

$$-\frac{\hbar^2}{2M} \sum_j \int \Psi_{\text{ion},\beta'}^* \Psi_{\text{ion},\alpha}^* (\nabla^2_{R_j} \Psi_{\text{ion},\alpha}) \Psi_{\text{ion},\beta'} \text{d}r_{\text{ion}} \text{d}r_{\text{ion}}^*.$$  \hspace{1cm} (3.22a)

$$-2 \frac{\hbar^2}{2M} \sum_j \int \Psi_{\text{ion},\beta'}^* \Psi_{\text{ion},\alpha}^* \left( \nabla_{R_j} \Psi_{\text{ion},\alpha} \right) \left( \nabla_{R_j} \Psi_{\text{ion},\beta'} \right) \text{d}r_{\text{ion}} \text{d}r_{\text{ion}}^*.$$  \hspace{1cm} (3.22b)

Although the non-diagonal matrix elements are small, they are crucial for understanding the electron scattering under the emission or absorption of a phonon.

Suppose that the electron wave function, $\Psi_{\text{ion},\alpha}$, can be expanded in a rapidly converging series in powers of $u_j$. Since $\nabla_{R_j} = \nabla u_j$, a linear expansion is sufficient to yield a contribution from the term in Eq. (3.22b). Ordinary perturbation theory gives

$$\Psi_{\text{ion},\alpha} = \Psi_{\text{ion},\alpha}^* + \sum_{\alpha', j} \left\{ \left( \Psi_{\text{ion},\alpha}^* \right)^* \left[ U_e(r, R_j^0 + u_j) - U_e(r, R_j^0) \right] \Psi_{\text{ion},\alpha} \right\} \text{d}r_{\text{ion}} \text{d}r_{\text{ion}}^*.$$  \hspace{1cm} (3.23)

$\Psi_{\text{ion},\alpha}$ is the wave function for the conduction electrons when the ions are at the equilibrium positions $R_j^0$. $U_e$ is an effective potential experienced by an electron which interacts with the ion core and with all of the other conduction electrons. Under the rigid-ion approximation,

$$U_e(r, R_j^0 + u_j) - U_e(r, R_j^0) = -u_j \cdot \nabla_r V(r - R_j^0),$$  \hspace{1cm} (3.24)

where $V$ is the rigid potential for the ion. Now the non-diagonal matrix element can be written as
\[
\langle \alpha', \beta' | H_{\text{total}} | \alpha, \beta \rangle = \frac{\hbar^2}{M} \sum_j \langle \beta' | \nabla_{\mathbf{r}_j} | \beta \rangle \frac{\langle \alpha' | \nabla_\mathbf{r} \mathbf{V}(\mathbf{r} - \mathbf{R}_j) | \alpha \rangle}{E_\alpha - E_{\alpha'}}.
\]

(3.25)

The transition between electron states $\alpha$ and $\alpha'$ take place under the absorption or emission of a phonon, i.e., $|E_\alpha - E_{\alpha'}| = \hbar \omega_{\beta'\beta}$. The matrix element between the phonon states in Eq. (3.25) can be rewritten as

\[
\langle \beta' | \nabla_{\mathbf{R}_j} | \beta \rangle = -\frac{M}{\hbar^2} (E_{\beta'} - E_{\beta}) \langle \beta' | \mathbf{u} | \beta \rangle.
\]

(3.26)

Since the energy is conserved in a scattering process, i.e., $E_\alpha - E_{\alpha'} = E_{\beta'} - E_{\beta}$, we finally arrive at the non-diagonal matrix element

\[
\langle \alpha', \beta' | H_{\text{total}} | \alpha, \beta \rangle = \sum_j \langle \beta' | \mathbf{u} | \beta \rangle \langle \alpha' | \nabla_\mathbf{r} \mathbf{V}(\mathbf{r} - \mathbf{R}_j) | \alpha \rangle.
\]

(3.27)

The matrix element in Eq. (3.27) can be calculated directly by considering separately the processes that involve the absorption and emission of a phonon $(q, \lambda)$ ($q$ is the phonon wave vector and $\lambda$ is phonon branch index). The electronic wave function is allowed to be a Bloch state $\Psi_{k}^\prime (\Psi_{k}')$. The calculated matrix element for the phonon absorption process is

\[
-\left[ \frac{\hbar}{2MN \omega(q, \lambda)} \right]^{1/2} \mathbf{e}(q, \lambda) \hat{I}(k, k) \left[ n(q, \lambda) \right]^{1/2} \delta_{q' - k, k, \mathbf{G}}.
\]

(3.28)

Where $\hat{I}(k, k)$ is

\[
\frac{1}{\Omega_a} \int \Psi_{k}^\prime (\mathbf{r} - \mathbf{R}_j) \nabla_\mathbf{r} \mathbf{V}(\mathbf{r} - \mathbf{R}_j) \Psi_k (\mathbf{r} - \mathbf{R}_j) d^3(\mathbf{r} - \mathbf{R}_j).
\]

(3.29)

The integration in Eq. (3.29) goes over the entire crystal volume and $\Psi_k / \sqrt{\Omega_a}$ is normalized to unity over an atomic cell. In Eq. (3.28), $\omega(q, \lambda)$ is the phonon frequency, $\mathbf{e}(q, \lambda)$ is the phonon polarization vector (of unit length), $n(q, \lambda)$ is the phonon population and is equal to $\left\{ \exp[\hbar \omega(q, \lambda) / k_B T] - 1 \right\}^{-1}$. The matrix element for the phonon emission process can similarly be calculated as
\[
- \left[ \frac{\hbar}{2MN\omega(q, \lambda)} \right]^{1/2} \epsilon(q, \lambda) \mathcal{I}(k, k') \left[ n(q, \lambda) + 1 \right]^{1/2} \delta_{q-k-k, G}. \tag{3.30}
\]

For the sake of convenience, a coupling function in reciprocal space is introduced and is defined by
\[
g(k, k'; \lambda) = - \left[ \frac{\hbar}{2MN\omega(q, \lambda)} \right]^{1/2} \epsilon(q, \lambda) \mathcal{I}(k, k'). \tag{3.31}
\]

The coupling function \( g(k, k'; \lambda) \) refers to the scattering from an electron state \( k \) to another state \( k' \) by absorption of emission of a phonon \( (q, \lambda) \).

An important parameter in e-ph coupling is the scattering rate, which is directly related to the e-ph coupling strength. The scattering rate is characterized by the quasiparticle lifetime \( \tau(k) \), which is given by
\[
\frac{1}{\tau(k)} = \frac{2\pi}{\hbar^2} \sum_{k, \lambda} \left| g(k, k'; \lambda) \right|^2 \times \{ \{ f(E_k) + n(q, \lambda) \} \delta(E_k - E_k + \hbar \omega(q, \lambda)) \} \delta_{k-k, G} + \{ 1 + n(q, \lambda) - f(E_k) \} \delta(E_k - E_k - \hbar \omega(q, \lambda)) \}, \tag{3.32}
\]
where \( f \) is the Fermi-Dirac function. The first (second) term in the bracket corresponds to phonon absorption (emission) process, respectively.

Very often in literatures, we see the Eliashberg coupling function \( \alpha^2 F(\omega) \). It is defined by
\[
\alpha^2 F(\omega) = \frac{V}{\hbar(2\pi)^3} \sum_{k, \lambda} \int_{S_F} \frac{d^2k}{V_k} \int_{S_F} \frac{d^2k'}{V_{k'}} \left| g(k, k'; \lambda) \right|^2 \delta(\hbar \omega - \hbar \omega(q, \lambda)) \int_{S_F} \frac{d^2k}{V_k}, \tag{3.33}
\]
where the surface integrals are over the Fermi surface \( S_F \). It is obvious from the definition that the Eliashberg coupling function gives the momentum averaged electron-phonon coupling on the Fermi surface.

Strictly speaking, many-body character should be taken into account in the calculation of electron-phonon coupling. In the context of many-body physics, the electron-phonon interaction gives rise to an additional term in the electron self-energy \( \Sigma_{e-ph}(\omega, \mathbf{p}, T) \). For an isotropic system, the electron-phonon part of the electron self-energy can be written as
\[
\text{Re} \Sigma_{e-ph}(\omega; T) = \int_{-\infty}^{\infty} d\nu \int_{0}^{\omega_{\text{max}}} d\omega' \alpha^{2} F(\omega') \left[ \frac{1 - f(\nu)}{\omega - \omega' - \nu} + \frac{f(\nu)}{\omega + \omega' - \nu} \right]. \tag{3.34a}
\]

\[
\left| \text{Im} \Sigma_{e-ph}(\omega; T) \right| = \pi \hbar \int_{0}^{\omega_{\text{max}}} d\omega' \alpha^{2} F(\omega') \left[ 1 - f(\omega - \omega') + 2\eta(\omega') + f(\omega + \omega') \right]. \tag{3.34b}
\]

### 3.3.2 Measuring e-ph Coupling by ARPES

ARPES can measure the spectral function of the electron, which is directly related to the electron self-energy. The electron-phonon part of the self-energy, \( \Sigma_{e-ph}(\omega; T) \), exhibits a dramatic change near the energy \(-\omega_{\text{max}}\) (\(\omega_{\text{max}}\) is the maximum phonon energy and zero is Fermi energy). A sudden change in the electron self-energy indicates an abrupt modification, or a “kink”, of band dispersion relation near this energy range.

This phonon kink has been observed in a variety of systems. Fig. 3.8 shows such a kink that was observed in the Be(0001) surface state. The band dispersion relation of the Be(0001) surface state exhibits an apparent discontinuity at -70 meV. In addition, the peak width becomes much narrower when the electron energy is higher than -70 meV. Fig. 3.9 shows the electron-phonon part of the self-energy, which was obtained through a fit to the experimental data in Fig. 3.8 using the Eqs. (3.34a) and (3.34b). \( \text{Re} \Sigma_{e-ph}(\omega) \) has a sharp peak at \(-\omega_{\text{max}}\), in accord with the discontinuity of the band dispersion relation. \( \text{Im} \Sigma_{e-ph}(\omega) \) is a constant at energy below \(-\omega_{\text{max}}\) and rapidly drops to zero at the Fermi level, which explains the sharpening of the SS peak near the Fermi level.

Another way of studying e-ph coupling by ARPES is to look at the temperature dependence of the peak width. The peak width is directly related to the imaginary part of the self-energy, i.e., the e-ph scattering rate. As the temperature gets higher, the phonon population, \( \eta(\mathbf{q}, \lambda) \), increases (Eqs. (3.32) and (3.34b)), leading to a broadening of the peak width. Fig. 3.10 shows an example of such a study, once again using the Be(0001) surface state [16]. The Eliashberg coupling function, under the Debye model, is \( \lambda \omega^{2} / \omega_{D}^{2} \), where \( \lambda \) is known as the electron-phonon mass enhancement parameter. The value of \( \lambda \) is a direct indication of the e-ph coupling strength in the material. Eq (3.34b) can be rewritten as
\[ |\text{Im} \Sigma_{\text{e-ph}}(\omega; T)| = 2\pi \int_0^{\omega_{\text{max}}} \lambda \left( \frac{\omega}{\omega_b} \right)^2 \left[ 1 - f(\omega - \omega') + 2n(\omega') \right] + f(\omega + \omega') \mathcal{H} \omega' \]

(3.35)

\[ \lambda \text{ can be obtained by fitting the peak width as a function of the temperature } T \text{ with Eq. (3.35) (dashed curve in Fig. 3.10). If the temperature is much larger than the Debye temperature, Eq. (3.35) can be further simplified as} \]

\[ \lambda = \frac{1}{2\pi k_b} \frac{d\Delta E}{dT}, \]

(3.36)

where \( \Delta E \) is the peak width at temperature \( T \) (straight line in Fig. 3.10).

The two methods discussed above have been applied to study e-ph coupling in a variety of 2D materials, including QWS in metallic films, graphene/graphite, etc. [17]. Chapter 6 will report on a new method of characterizing e-ph coupling by ARPES. More specifically, the ARPES spectra at regions far away from the direct transition show gaps induced by e-ph coupling. A more detailed discussion of these phonon-induced gaps will be presented in chapter 6.

REFERENCES

[8] The Huygens-Fresnel principle applies to wave propagation in general. In the present context, it states that the transmitted wave has a definitive phase relative to the incident wave, as long as the transmitted wave is propagating.
FIGURES

Figure 3.1. (a) Allowed electronic states in momentum space for a free-electron-like thin metal film. (b) Expected band dispersion relations observed in ARPES.

Figure 3.2. Thin film as a Fabry-Pérot interferometer. The initial state undergoes multiple reflections to form QWS. After photoexcitation, the electron is excited into a time-reversed low-energy electron diffraction (TRLEED) state and then enters the detector to complete the electrical circuit.
Figure 3.3. Quasi-freestanding Pb films grown on HOPG. (a) Normal emission spectra at various nominal Pb coverages. (b) Experimental and fitted energies of QWS as a function of film thickness. (c) Phase shift at the surface and interface.
Figure 3.4. (a) Intensity evolution of QWS peaks for different film thicknesses as a function of the nominal Pb film coverage. (b) Relative surface energies as a function of film thickness for freestanding Pb films, based on a first-principles calculation.
Figure 3.5. Conjugate van Hove-type singularities near the Si band edge at the Pb-Si(111) interface. (a) Phase shift and (b) reflectivity plotted as a function of electron energy. $E_0$ is the Si valence band edge. The diamonds are experimental data points, obtained by measuring the QWS of Pb films grown on various Au-terminated Si(111) surfaces. The solid curves are fits, and the dotted curves are extrapolations of the fits.
Figure 3.6. Schematic potential in the vicinity of a crystal surface, adapted from [10]. Surface states arise through multiple reflections between the terminating plane of the crystal and the surface barrier.

Figure 3.7. Wave function of a Shockley surface state (top), a quantum well state (middle), and a quantum well resonance (bottom). The plotted wave functions mimic the real electron wave functions for a 16 ML Ag(111) film ($k_z$ close to L point for QWS and QW resonance). The beating patterns in the wave functions of QWS and QW resonance are caused by the electron wave mixings near the L point.
Figure 3.8. The phonon kink in the Be(0001) surface state, adapted from [14]. The spectra are measured along the $\Gamma M'$ direction ([112]).
Figure 3.9. Plot of the electron-phonon part of the self-energy, $\Sigma_{e-ph}(\omega)$, for the Be(0001) surface state electron [15]. The self-energy is obtained through a fit to the ARPES data. The experimentally derived maximum phonon energy is 70 meV (indicated by a stick), and the coupling parameter $\lambda$ equals 1.18.

Figure 3.10. Deducing the electron-phonon coupling strength by temperature dependence of the peak width of the Be(0001) surface state [16]. Open circles are for increasing temperature and the filled circles are for decreasing temperature. The solid curve and dashed curve are fits to the experimental data, using Eq. (3.35) and (3.36), respectively.
4 Interface-Induced Interference in Ag/Ge(111)

4.1 Introduction
Thin film is grown on a substrate, whose lattice constant generally differs from that of the film. Conventionally, the substrate effect on the electronic states of the films is taken into account by using a phase shift and reflectivity at the interface, both of which were discussed in the previous chapter. However, the substrate effect is not that simple. As a result of the mismatched lattice, the electrons would experience two distinct periodic potentials near the interface. The incommensurate potential at the interface could give rise to significant complexity in the electronic structures of the films. This chapter will focus on the studies of Ag films grown on Ge(111), a prototypical metal-semiconductor system that has simple and well-understood components. The combined system, however, reveals rich electronic structure. More specifically, the Fermi surface reveals intricate patterns that resemble interfering waves emanating from multiple centers. We will show that this is a direct result of electron wave mixing by the incommensurate interface potential [1].

This chapter is organized as follows: a brief introduction to previous works on this system will be presented (Sec. 4.2). Our experimental results will be discussed in Section 4.3. A model calculation that incorporates the incommensurate interface scattering will be presented and compared with the experiment (Sec. 4.4). Finally, the thickness dependence will be studied (Sec. 4.5), which reveals a $1/N$ ($N$ is the film thickness) dependence of the interaction strength from the interface potential.

4.2 Previous Studies
The successful fabrication of highly uniform Ag films on Ge(111) is a prerequisite for the current study. When a low temperature deposition is followed by a careful annealing procedure, atomically uniform Ag films can be grown on Ge(111) [2,3]. Ag and Ge do not intermix and react in an appreciable manner, which results in an abrupt interface. The Ag films, with bulk-like lattice constant, are oriented with the crystallographic axes parallel to the corresponding ones in the Ge substrate [2].
Previous studies have shown that new sets of quasi-particle states emerge as a result of the Ag-Ge interface scattering \([4,5]\). These states are centered at the \(\overline{M}\) point of Ge (not Ag) and have band spacing about half of the normal quantum well states (Fig. 4.1). These quasi-particle states appear as smooth parabolic bands and no fine interference structures can be resolved in these previous studies. With improved sample quality, we will see later that these states actually exhibit zigzag patterns with multiple energy gaps, which indicates a strong electronic interference effect. This electronic interference arises as a result of electron wave mixing by the interface potential, and give rise to significant complexity in the Fermi surface, as revealed by our three-dimensional band structure mapping.

### 4.3 Three-Dimensional Band Structure Mapping

Angle-resolved photoemission measures the spectral function as a function of two in-plane wave vectors \((k_x, k_y)\) and the energy \((E)\). In order to investigate the fine electronic interference structures, a large momentum (and energy) space is probed. Using modern electron analyzer equipped with a two-dimensional detector, we can obtain dispersion relations of energy versus in-plane momentum along a selected direction in a single scan. The angular range in one scan is about 10º and therefore covers a line in the reciprocal space, whose length is about one-fifth of reciprocal lattice vector (for 50 eV photons). Spectra must be taken at various rotation angles of the sample in order to generate the three dimensional spectral function \(A(k_x, k_y, E)\). Although the experiment is quite straightforward, a smart algorithm is needed to obtain a smooth spectral function \(A(k_x, k_y, E)\) from many overlapping spectra taken at various sample angles. Our algorithm uses the linearly weighted average for each point \((k_x, k_y, E)\). The experimental geometry for Fermi surface mapping is shown in Appendix B.

An overview of the results from a uniform film thickness of 9 atomic monolayers (ML) is displayed in Fig. 4.2 using various planar cuts. On the left, two vertical cuts separated by 90º, one with in-plane momentum along \(\overline{\Gamma M}\) (x direction) and the other along \(\overline{\Gamma K}\) (y direction), reveal energy dispersion relations \(E(k_x)\) and \(E(k_y)\) along these high-symmetry directions. The spectral features are dominated by roughly parabolic bands centered at the zone center \(\overline{\Gamma}\). These are the usual quantum-well subbands that are derived from the free-electron-like \(sp\) electrons in Ag \([6]\). Upon closer inspection, one can see kinks in these dispersion relations. These kinks occur at the band edges of Ge and are caused by hybridization of the Ag electron wave functions.
with those in the Ge below the band gap \([3,7]\). In contrast to the \(\Gamma K\) direction, the dispersion relations along the \(\Gamma M\) direction display much richer structures near the Fermi level where the subbands develop gaps and become cross-linked. These features, which arise from incommensurate interface potential, will be discussed in more detail later.

Additional insight can be obtained through investigation of the constant-energy contours that are displayed on the right-hand side of Fig. 4.2. At energies far below the Fermi level (-2.4 eV), the contours are nearly circular near the zone center and become hexagonal in shape as the in-plane momentum increases. This is to be expected based on the standard quantum-well model: the dispersion relations of the subbands are nearly free-electron-like, but are anisotropic due to the crystal potential. This gradual change of the contour is confirmed by our calculation (Fig. 4.3). The calculation employed the usual Bohr-Sommerfeld quantization condition \([8]\),

\[
(k_{1z} - k_{2z})(Nt + 2\Delta) = 2n\pi,
\]

where \(k_{1z}\) and \(k_{2z}\) are the wave vectors of the two Bloch states, one traveling toward the surface, and the other reflected from the surface, that combine to form a standing wave in the film; \(N\) is the film thickness in monolayers, \(t\) is the monolayer thickness, \(n\) is a quantum number, and \(\Delta\) is the average charge spillage parameter that accounts for the finite barriers at each boundary \([8]\). The band structure of Ag in this calculation was taken from an empirical model \([9]\).

Furthermore, the quantum well contours exhibit intensity modulations and fine structures that track closely the Ge band edge. One such example is illustrated in Fig. 4.4. The second innermost quantum well contour shows strong intensity modulations and the spectral weight appears to be pushed towards the outside of the Ge band edge (blue curves). These fine structures, which arise from the electronic interaction between the film and substrate, are in line with the “kinks” observed in energy dispersion relations. A detailed analysis of such fine structures in full momentum space could allow for an accurate determination of the Ge band edge \([3]\), which therefore suggests a method for probing the band structure of the 3D solid. The present method is particularly useful for exacting the band edge of the semiconductor.

### 4.4 Interface-Induced Electronic Interference Structures

This section will examine the quasiparticle states caused by the Ag-Ge interface potential. A close-up of the dispersion relations near the Fermi level around the Ge \(\overline{M}\) point is shown in Fig.
4.5(a). Although the spectral function exhibits the usual quantum well states at lower energies (below -1.5 eV), it becomes substantially more complicated at higher energies with multiple gaps in the subband dispersion relations and cross-linking segments. The complexity is further illustrated in Fig. 4.5(c), in which the second derivative of the data along the energy axis is presented. The differentiation sharpens the spectral features and removes the smooth background, which makes it easier to follow the spectral peaks. The results show zigzag dispersion relations and multiple anticrossing energy gaps, indicating that there exists an interference coupling among the various quantum-well states.

In order to explain these observations in detail, we performed a calculation that incorporates the essential components of the electronic structure of the system; bulk band structure, confinement, and scattering by the interface potential. Two sets of basis wave functions are included; one set is the subband quantum-well wave function $\psi_{n,k}$, and the other set is $\psi_{n,k-g}$, where $k$ is an arbitrary in-plane wave vector and $g$ is a reciprocal lattice vector of the Ge surface. These two sets intermix by the interface potential $U$, which has a periodicity determined by $g$ and is spatially localized near the interface. The coupling matrix element

$$M_{m,i} = \langle \psi_{m,k-g} | U | \psi_{i,k} \rangle$$

(4.2)

is assumed to be the same for all subbands $m$ and $n$ over the regions of interest. The diagonal part of the Hamiltonian is constructed from the known subband dispersion relations, and the off-diagonal matrix element $M = M_{m,i}$ is treated as an adjustable parameter. Finally, the Hamiltonian of the system can be written as

$$H =
\begin{bmatrix}
E_{1,k} & 0 & 0 & 0 \\
0 & E_{2,k} & 0 & 0 \\
0 & 0 & \cdots & 0 \\
0 & 0 & 0 & E_{n,k}
\end{bmatrix}
+ \begin{bmatrix}
M \\
M \\
M \\
M
\end{bmatrix}
+ \begin{bmatrix}
E_{1,k-g} & 0 & 0 & 0 \\
0 & E_{2,k-g} & 0 & 0 \\
0 & 0 & \cdots & 0 \\
0 & 0 & 0 & E_{n,k-g}
\end{bmatrix}.$$
where $E_{n,k}$ and $E_{n,k-g}$ are energy eigenvalues of quantum-well states $\psi_{n,k}$ and $\psi_{n,k-g}$, respectively. Note that the diagonal matrix element for interface potential $U$ is always zero ($\langle \psi_{m,k} | U | \psi_{l,k} \rangle = 0$), which is required by the periodicity of the interface potential.

Diagonalization of the Hamiltonian, with $M$ set to 0.15 eV, yields the green curves in Figs. 4.5(b) and 4.5(c), where they are compared to the original data and second derivative of the data, respectively. The observed zigzag dispersion relations and multiple energy gaps are well-reproduced by the calculation. Although a similar model was discussed earlier [5], no zigzag patterns or gaps characteristic of the interference effects were observed experimentally in that work.

A much more stringent test of the above model is to compare the calculations to the three-dimensional data set at various energies. An example presented in Fig. 4.6(a) shows the constant-energy contours of the second-order differentiated data at -0.4 eV. The results reveal the details of the six secondary sets of rings intersecting the primary set centered at $\Gamma$. The calculated constant-energy contours are superimposed on the data in Fig. 4.6(b). An enlarged view of the bottom secondary ring structure is presented in Fig. 4.6(c) for a detailed comparison. The calculated ring shapes and positions are in excellent agreement with the experiment. More specifically, the innermost ring in Fig. 4.6(c) has an hourglass shape, and the second ring has a number of wiggles. These subtle features are a direct consequence of the interference of the quantum well states caused by the coupling matrix $M$ in Eq. (4.2), as can be easily verified by setting $M$ to zero in the calculation. With $M = 0.15$ eV from our analysis, the anticrossing gaps are about $2M = 0.3$ eV. One of the gaps in Fig. 4.5(b) is indicated by a vertical (cyan) bar of a height of 0.3 eV.

To recap, we observed complex electronic interference structures in atomically uniform Ag films on Ge(111), which are a direct consequence of electronic coupling by the interface potential. The next step is to explore further and investigate the physical meaning of the coupling matrix $M$.

### 4.5 Thickness Dependence Study

As the interface potential $U$ in Eq. (4.2) is limited spatially to about one atomic layer at the interface, the matrix element $M$ is expected to scale as the inverse film thickness, or $1/N$. In order
to verify this point, we measured the spectral function along the $\Gamma M$ direction for a number of different Ag film thicknesses. The results are summarized in Fig. 4.7. The original data is presented here, instead of the second derivatives. Also shown are results of the same fitting analysis of the band dispersion relations, as indicated by the solid (green) curves. For each case, a vertical (cyan) bar is included, which corresponds to $2M$, or the anticrossing gap. It is apparent that this gap decreases as the film thickness $N$ increases.

The matrix element $M$ deduced from the fits for various thicknesses is shown in Fig. 4.8. The curve is a fit based on the functional form $C/N$, which describes the data well. Therefore, the matrix element $M$ follows the trend expected from the model. The constant $C$ is the coupling matrix element for 1 ML film and therefore can be understood as the Fourier component of the interface potential. The constant $C$ deduced from the fit is 1.55 eV, which is within the range of typical crystal potential. For example, the Fourier component of Ge crystal potential is typically between 3 eV and 0.8 eV, depending on the vector type [10]. In practice, it is difficult to determine the value of $C$ a priori, due to the structural complexities near the interface. Nevertheless, the constant $C$ provides a direct measure of the strength of the interface potential.

4.6 Conclusions

The essential physics of the interference pattern in this system is the coupling caused by the interface potential. In our model, the effects of the Ag lattice and quantum confinement are included in the basis wave functions $\psi_{n,k}$ and $\psi_{n,k-g}$ for the quantum well states. Coupling by the incommensurate interface potential makes the system aperiodic, and strictly speaking, the wave vector $k$ is not a good quantum number. Nevertheless, the observed spectral function can be well-described in terms of intermixing of the basic Bloch states, as demonstrated by our calculation. The case is somewhat akin to quasicrystals, which also lack spatial periodicity [11,12,13]. The present work shows that incommensurate scattering at the interface can cause substantial complexity in the electronic structure of thin films near the Fermi level, where electronic transport dominates. As commensurate interfaces are few (or nonexistent), the phenomenon presented in this study is expected to be a ubiquitous feature of metal-semiconductor systems.
REFERENCES


Figure 4.1. ARPES spectra of a 13 ML Ag film on Ge(111) measured along the $\Gamma\bar{M}$ direction ([11\overline{2}] direction) at 50 eV photon energy [4]. The approximately parabolic bands at normal emission are normal quantum well states. The quasiparticle states derived from the incommensurate interface scattering are centered at the $\bar{M}$ point of Ge, instead of Ag.
Figure 4.2. Photoemission intensities measured from an atomically uniform Ag film of 9 ML thickness on Ge(111). Various cuts of the three-dimensional data show energy-versus-momentum dispersion relations (left) and constant-energy contours (right) as labeled. The contour plots are oriented with the $x$ axis pointing to the right and the $y$ axis pointing upward. The photon energy used was 50 eV.
Figure 4.3. Constant-energy contour at -2.4 eV from a 9 ML Ag film on Ge(111), compared with a model calculation (green curves). See the text for details of the calculation.

Figure 4.4. Intensity modulations and fine structures in QW contours (at -1 eV from a 9 ML Ag film) caused by coupling with the substrate. The Ge band edge, obtained from empirical pseudopotential calculations [10], is shown as blue curves.
Figure 4.5. (a) ARPES spectra along the $\Gamma \bar{M}$ direction ($[1\bar{1}2]$) from a 9 ML Ag film on Ge(111). (b) Spectra compared with a model calculation (green curves). The cyan bar indicates the size of the anticrossing gap. (c) The second derivative of the spectra compared with the model calculation (green curves).
Figure 4.6. (a) Constant-energy cut at -0.4 eV through the second derivative of the three-dimensional data set. (b) The same data compared with calculation (green curves). (c) An enlarged view of the ring structure centered at the bottom Ge $\bar{M}$ point.
Figure 4.7. Photoemission data along $\Gamma\bar{M}$ ([112]) for $N = 4, 5, 6, 9, 13$ and 18 ML Ag films on Ge(111). The solid curves (green color) are fits to the band dispersions. The vertical bars (cyan color) indicate the size of the anticrossing gap in each case.
Figure 4.8. Coupling matrix element $M$ as a function of film thickness. The curve, which is proportional to $1/N$, is a fit.
5 Coherent Grating Cavity Modes in Corrugated Films

5.1 Introduction

Controlled modification of material structures at the nanoscale is a key concept underlying advanced applications and device designs. Crystal surfaces oriented at a small angle relative to a close packed atomic plane may exhibit a periodic array of atomic steps; such stepped surfaces represent an important class of templates for periodic atomic-scale modulation. Such periodically modulated substrates could significantly alter the electronic structures of thin films grown on them and thereby provide an opportunity to tune the properties of thin films. In addition, the existence of the steps might give rise to electronic localization along the direction perpendicular to the step edges and result in quasi-1D electron system (stripes). While a strictly 1D material largely remains a theoretical construct, such systems could be interesting test cases for theoretical predictions.

This chapter will present an ARPES study of Ag and Pb corrugated films grown on the Si(557)-Au surface. The Si(557)-Au surface has a well-ordered step structure and allows for the growth of regularly corrugated Ag and Pb films [1]. The electronic structures of flat Ag and Pb films have been previously measured by ARPES, which provide good references for investigating the effects of the corrugation [2,3]. Our results show that the corrugation modulates the electron motion and thus modifies the electronic properties of the films [4]. More specifically, the valence electrons form coherent grating cavity modes which are defined by the corrugation geometry.

This chapter is organized as follows: First, a brief review of previous works on the stepped surface (also called vicinal surface) will be provided (Sec. 5.2). The experimental results from corrugated Ag and Pb films will be discussed in Sec. 5.3 and 5.4, respectively. Sec. 5.5 will discuss the initial states (real electronic states) in these films, i.e., coherent electronic grating cavity modes. The variations of photoemission pattern as a result of photon energy are attributed to final state effects, i.e., effects that are caused by the photoemission process. Finally, some future experiments will be discussed in Sec. 5.7.
5.2 One-Dimensional vs Two-Dimensional

Most previous works on the subject of stepped surface have focused on the surface state (SS), because SS is strongly modulated by the steps and can be easily probed by ARPES and STM. There are two popular systems for this study, i.e., vicinal metal substrates and atomic chains grown on miscut Si(111) substrates [5,6,7]. The central question is the dimensionality of the surface state. In some cases, the SS electrons are free to propagate across the steps, thus forming Bloch-like waves (2-dimensional). A more interesting situation would be that electrons are confined by steps to form localized states (1-dimensional). This possibility of creating 1D electron gas has attracted considerable interest, since many exotic physics have been predicted for 1D electron system [8].

One-dimensional systems are particularly interesting for theorists, because this is the lowest dimension that still allows for translational motion and the mathematics is generally much simpler than is the case for higher dimensions. Nevertheless, the interaction of electrons in 1D is far from trivial [8]. In fact, electrons interact so strongly in one dimension that the single-electron concept breaks down and gives away to collective excitations. This strong interaction is a direct consequence of the reduced dimension, where electrons cannot avoid each other when moving. As a result, a single excited electron causes a domino effect that excites all of the other electrons. One of the most counterintuitive predictions for 1D electron gas is the so-called “spin-charge separation”. It states that electrons in 1D are split into two independent “quasiparticles”, the spinon and the holon, which carry the spin and charge of electrons, respectively. The resulting band dispersion, if it were measured through ARPES, would be two split bands (the holon and the spinon band) crossing at the Fermi level (Fig. 5.1(a)). Fig. 5.1(b) shows the propagation of the holon and spinon in real space, after the creation of a photohole from photoemission. The hole decomposes into two collective excitations, the holon and spinon. The holon carries the charge of the hole but is spinless, while the spin is carried by the spinon. Holon and spinon have different group velocities, which leads to the separation of spin and charge. A hole in the top row of Fig. 5.1(b) separates into a holon and spinon in subsequent rows via the hopping of electrons into empty sites (curved red arrows). The holon is an unoccupied site between opposite spins, and the spinon corresponds to a pair of adjacent parallel spins, i.e., an antiferromagnetic domain boundary. While the holon propagates by this hopping process, the spinon moves by an exchange between adjacent spins. These two mechanisms explain the two
different velocities of the holon and the spinon. As the holon and spinon approach the Fermi level, they become narrower and eventually converge to the same Fermi wave vector. The excitation energy vanishes right at the Fermi level, causing the holon and the spinon to recombine into a normal hole.

Despite of the beauty of this theory, spin-charge separation has remained elusive to experimentalists due to lack of truly 1D system. Recent ARPES studies provide evidence of spin-charge separation in the organic conductor TTF-TCNQ and cuprates \cite{9,10}. Nevertheless, there has been no clear evidence of spin-charge separation for SS on vicinal surfaces.

The critical proof of a 1D system is the lack of electronic dispersion within the plane perpendicular to the chain. ARPES can directly map the band structure and therefore provide a direct test for any possible 1D system. An ARPES measurement of a Si(553)-Au chain is shown in Fig. 5.2 \cite{11}. The Fermi surface (Fig. 5.2(b)) consists of weakly wiggling lines along the $y$ direction (perpendicular to the chains), which indicates the quasi-1D nature of electrons. However, surface state on many other vicinal surfaces exhibit 2D behaviors, even though their surface structures appear to be of 1D-like chains. For example, the photoemission spectra for Cu(443), as shown in Fig. 5.3, reveal parabolic surface states centered at the Brillouin zone (BZ) boundaries of the step modulation \cite{12}. The positions of the SSs do not change with varying photon energy, indicating that the SS is quantized along the optical normal direction and is coherent across the steps. As the photon energy increases, the probed $k_z$ changes from $G_{111}$ to $G_{222}$, which explains the gradual shift of the spectral weight from the left parabola to the right one. A more detailed discussion of this behavior of SS will be given in Sec. 5.5.

Although most of previous works primarily concern the SS on a vicinal substrate, a recent ARPES study of corrugated Ag films, grown on Si(111)-(4X1)-In chain structures, shows that the quantum well states of the Ag films exhibit surprising quasi-1D dispersion \cite{14}. A slightly miscut Si(111) substrate was employed in this study to form single-domain Si(111)-(4X1)-In chain structures (chain direction is parallel to the step edge). The QWS in the Ag films, as shown in Fig. 5.4, reveals parabolic band dispersion along the direction parallel to the chains and almost no dispersion along the direction perpendicular to the steps. This indicates that QWSs are localized along the direction perpendicular to steps, and therefore can be regarded as quasi-1D. It is also proposed that the stacking fault in the Ag films, which is caused by the lattice mismatch
between the Ag films and the Si(111)-(4X1)-In chain structures, is the origin of the electronic localization.

### 5.3 Ag Films on Si(557)-Au

Our goal is to conduct a comprehensive study of corrugated metal films grown on vicinal substrates, including photon energy dependence and a large $k$-space mapping, and to investigate the dimensionality of the QWS. The present work employs the vicinal Si(557) surface as the base substrate, which consists of (111) terraces separated by steps. Plain Si(557), 9.5° miscut towards $\overline{112}$ direction from Si(111), can be prone to the formation of mixed single and triple steps. Dosing the surface with 0.2 atomic layers of Au stabilizes the single steps and yields a well-ordered step array at a period of $\lambda = 19.1$ Å [1]. On this Si(557)-Au surface, we deposit Ag at 50 K and then anneal to 300 K to form corrugated Ag films [2]. The films are oriented crystallographically in parallel with the substrate and have bulklike lattice constants based on reflection high-energy electron-diffraction (RHEED) measurements. The same measurements reveal superlattice diffraction peaks indicating a well-ordered step structure for the Si(557)-Au surface before film growth and a corrugated film structure of the Ag overlayers comprising (111) sections periodically offset by the substrate steps (Fig. 5.5(b)). Angle-resolved photoemission measurements were performed at the Synchrotron Radiation Center using linearly polarized light (with the electric field vector oriented at 30° relative to the surface normal at normal emission). The energy resolution was ~20 meV, and the substrate was kept at 50 K during the measurements. Spectra were also taken at room temperature for comparison; the results were quite similar.

Fig. 5.5(a) is a schematic view of the experimental configuration. The surface normal Si[557] is at a miscut angle $\alpha = 9.45$° relative to the Si(111) terrace normal. The $+x$-axis is defined to point along Si[1710], the stepping-down direction of the Si substrate. The results of band structure mapping along the $x$ direction at various photon energies for a 15 ML corrugated Ag film are shown in Fig. 5.6. The spectra at other film thicknesses of up to 50 ML are similar; the quantum well features become smeared out at higher thicknesses. Two sets of parabolic QWS bands can be clearly seen, but neither of them is centered along the Si[111] direction, or the optical normal (Si[557] direction). The physics becomes clearer when the spectra are plotted
as a function of the in-plane wave vector $k_x$, which is referenced to normal emission along Si[557] (Fig. 5.7). At low photon energies (11, 15, and 22 eV), the data show a set of parabolic quantum well subbands centered at $k_x = -g/2 = -0.164$ Å$^{-1}$, where $g = 2\pi/\lambda$ is the primitive reciprocal lattice vector corresponding to the step modulation. The very sharp feature right at the Fermi level is derived from the Ag(111) Shockley surface state. Another set of quantum well subbands centered at $k_x = -3g/2 = -0.493$ Å$^{-1}$ is observed at high photon energies (50, 78, and 90 eV). Both sets of subbands are present at intermediate photon energies. At 36 eV, the two overlapping sets are about equally intense, giving rise to the false impression of segments of nearly dispersionless subbands. Note that the gradual shift of spectral weight from one parabola to the other is roughly in line with the position change of Si[111] emission direction in $k$ space (slanted blue lines), i.e., the intensity of QWS set is approximately at its maximum when it coincides with the Si[111] emission direction in $k$ space. This correspondence is a direct consequence of blazed diffraction of the final state, which we shall discuss in details later (Sec. 5.6).

For smooth Ag films prepared on the on-axis Si(111), the band structure is much simpler. The films act as parallel-plate Fabry-Pérot interferometers, and the quantum well subbands appear as a set of parabolas centered about the surface normal, or the Si[111] direction, independent of the photon energy (Fig. 5.8). If all of the (111) sections in the corrugated film (see Fig. 5.5(a)) act independently, they should yield quantum well subbands centered about the [111] direction, possibly broadened by the finite section width. The slanted lines in Fig. 5.7 indicate this fixed Si[111] emission direction: $|k_x|$ increases smoothly for increasing photon energies. The data are inconsistent with this picture of independent (111) sections. Instead, the (111) sections should be closely coupled and act together as a single coherent quantum mechanical system. Another piece of evidence for this coherent coupling across the steps is the fact that the QWS bands are centered at the BZ boundaries of the step modulation (Fig. 5.7).

While the $sp$ band exhibits dramatic differences from their counterpart in flat films, the very localized $d$ bands behave similarly as those of Ag films on Si(111), only shifted by an emission angle close to the miscut (Fig. 5.9). The coherent length of $d$ band electrons in bulk Ag is typically ~30 Å, which is just comparable to the step periodicity $\lambda = 19.1$ Å [15]. The actual coherent length in the current system could be lower than 30 Å, due to the existence of steps.
This means that $d$ band electrons will lose their phase coherence when travelling between terraces. Therefore, it is not surprising that $d$ band electrons are localized within each terrace and act independently. It is interesting to note that the center of the $d$ bands is actually $\sim 2^\circ$ off the Si[111] direction (Fig. 5.9). If we assume that the center of $d$ bands is along the Ag[111] direction, this indicates that the Ag film might be slightly tilted with respect to the Si substrate. This tilting was first proposed by Nagai to explain the crystallographic tilt of heteroepitaxial semiconductor crystals grown on a vicinal substrate [16]. A recent study shows that this tilt exists even for oxide films grown on vicinal metal substrate [17]. A straightforward lattice matching allows one to calculate the tilt angle $\Delta \alpha$ as

$$\Delta \alpha = \tan^{-1}\left( \frac{a_s - a_f}{a_s} \tan \alpha \right),$$

(5.1)

where $a_s$ and $a_f$ are the step height for the substrate and film, respectively. $\alpha$ is the miscut angle of the substrate. For Ag films on Si(557)-Au, the calculated tilt angle $\Delta \alpha$ is $2.35^\circ$, very close to our result obtained from the $d$ band offset. Nevertheless, we should mention that the $d$ bands in Ag are quite complicated, and there could be some uncertainty associated with the actual value. More accurate measurements, e.g., surface X-ray scattering, are needed to confirm this tilt.

The fact that the QWSs from the $sp$ band are dispersionless with photon energies, i.e., their positions in $k$ space are fixed, indicates that the quantization of QWS is along the optical normal (Si[557]), instead of the Si[111] direction. The centers of the QWS bands are at the BZ boundaries of the step modulation, which suggests that this alignment is determined by the substrate and is independent of the film structure. In order to verify this point, we carried out similar experiments on Pb films grown on the same substrate.

### 5.4 Pb Films on Si(557)-Au

Following a previous recipe for growing atomically uniform Pb films on Si(111) [3], we successfully fabricated regularly corrugated Pb films on the Si(557)-Au surface. The band structure of Pb(111) film is more complex than that of Ag(111) film, because there are four valence electrons per atom (Fig. 5.10). Nevertheless, the band dispersion near the zone center is still parabolic, albeit a large effective mass.

The photoemission spectra of a 21 ML corrugated Pb film, measured along the direction perpendicular to the steps, is shown in Fig. 5.11. Nearly parabolic subbands centered about
\( k_x = - g/2 \) are observed at 21 eV, and a replica set centered about \( k_x = -3g/2 \) is observed at 50 and 70 eV. At 25 and 26 eV, the two overlapping sets are about equally intense. Again, the shift of spectral weight from the right set to the left one is approximately associated with the Si[111] emission direction in \( k \) space (blue slanted lines). Therefore, the overall behavior is similar to the Ag film case, except that the subband effective masses are substantially larger due to the different bulk band structure (Fig. 5.10). Although the lattice constant of Pb is ~25% larger than that of Ag, the subband alignment is again determined by the substrate's corrugation period. This provides critical evidence for our interpretation that the observed QWS is coherent across (111) terraces.

5.5 Coherent Grating Cavity Modes

To summarize, the key experimental observations are as follows:

(1) Positions of QWS subbands do not change with varying photon energies;
(2) QWS subbands are centered at the BZ boundaries of the step modulation;
(3) QWS intensities are approximately maximized when they coincide with the [111] emission direction in \( k \) space.

Interestingly, our results of QWS from corrugated films bear striking similarities to those of the surface state on vicinal metal substrates (compare Fig. 5.7 with Fig. 5.3). This behavior of SS is now well understood. As discussed in Sec. 5.2, this SS is quantized along the optical normal direction and is coherent across the steps. The alignment of the SS with the BZ boundaries of the step modulation can be derived from the projection of the SS momentum onto the surface Brillouin zone (see Fig. 5.3) [13,18]. The perpendicular momentum \( k_z \) (along [111] direction) of the Shockley surface state at L point is

\[
k_z = \frac{\pi}{t} \pm iq. \tag{5.2}
\]

where \( t \) is the interlayer spacing for the (111) film and \( q \) is the inverse of the decay length of the surface state. The projection of the real part of \( k_z \) onto the optical surface gives \( k_{\parallel} = \frac{\pi}{t} \sin \alpha \approx \frac{\pi \alpha}{t} \), which is exactly the BZ boundary of the step modulation (assuming single steps). The gradual shift of the spectral weight from one set of SS to the other with increasing
photon energy was attributed to the change in probed $k$ space as a result of photon energy variation. The SS set observed at lower (higher) photon energy originates from the L gap at $G_{111}/2$ ($3G_{111}/2$), respectively. Note that the SS of corrugated Ag films, which is the sharp feature right at the Fermi level, behaves identically to the SS on the vicinal metal substrate (Fig. 5.7).

This interpretation of SS alignment with BZ boundaries of step modulation is not applicable to QWS, because the perpendicular momentum of QWS can be any value between 0 and $\pi/t$, depending on the quantization condition. A direct projection of the perpendicular momentum of QWS onto the surface BZ would result in QWS bands centered at various points in $k$ space, which is apparently inconsistent with our experimental observation (2). Therefore, this behavior of QWS requires a more general understanding. After all, a surface state can be conceptually understood as a special quantum well state in the limit of zero film thickness.

Based on experimental observations (1) and (2), we know that QWSs are quantized along the optical normal direction and are coherent across the steps. This coherence allows for the electron wave mixing by the corrugation potential. Therefore, the standard quantization condition must be generalized to yield a pair of equations:

$$ (k_{z1} - k_{z2})D + \Phi = 2n\pi, \quad (5.3) $$

$$ E = E(k_x, k_{z1}) = E(k_x - jg, k_{z2}), \quad (5.4) $$

where $k_{z1}$ and $k_{z2}$ are the perpendicular wave vectors of the two counterpropagating Bloch states at the same energy $E$ that combine into a standing wave (Fig. 5.12(a)); $D$ is the film thickness, $\Phi$ is the total phase shift at the surface and interface, $n$ is the subband quantum number, and $j$ is an integer specifying the order of umklapp diffraction caused by the corrugation. Smooth films on the flat (111) surface support only specular reflections ($j = 0$). With the corrugation, the film becomes a one-dimensional cavity bounded by the surface and interface as two parallel gratings. Standing waves, or quantum well states, form in the cavity by two conjugate umklapp reflections, one at the interface with $\Delta k_x = jg$ and the other at the surface with $\Delta k_x = -jg$.

An additional grating condition, familiar from optics, places a strong limit on the available umklapp orders. Specifically, the surface and interface gratings are strongly blazed; therefore, only those diffraction orders that nearly satisfy the reflection geometry for each (111) facet are
important. The intensity of electron reflection from each (111) facet is given, within the Fraunhofer approximation, by

\[ I \propto \left( \frac{1}{2} b \Delta k_i \right)^2 \sin^2 \left( \frac{1}{2} b \Delta k_i \right), \]

(5.5)

where \( \Delta k_i \) is the change in wave vector within the (111) terrace plane and \( b = 18.8 \ \text{Å} = \lambda \) is the terrace width (Fig. 5.12(b)). This single-slit diffraction function is strongly peaked about the specular condition \( \Delta k_i = 0 \) with a full width of ~0.3 Å\(^{-1}\). Fig. 5.12(c) shows a plot of Eq. (5.5) with the different orders of the conjugate umklapp diffractions indicated for a typical subband minimum within the region of interest. It is evident that \( j = -1 \) is the only important order. This condition corresponds approximately to two counterpropagating Bloch waves along the [111] direction with \( k_x = \pm g/2 \). They satisfy both the blazing condition \( \Delta k_i \sim 0 \) and the conjugate diffraction conditions \( \Delta k_i = \pm g \) at the surface and interface.

For a detailed verification of the model, Fig. 5.13(a) shows the calculated subband dispersion relations of a 15 ML corrugated Ag film for \( j = -1 \). Also shown are the experimental data taken at 22 eV presented in the second derivative mode to enhance the contrast. The calculation involves the simultaneous solutions of Eqs. (5.3) and (5.4) with the bulk band structure \( E(k) \) of Ag taken from an empirical calculation [19]. The phase shift \( \Phi \) in Eq. (5.3), assumed to be a constant, is adjusted to approximately line up the calculation with the data. The agreement is very good; the slight discrepancy can be attributed to variations of \( \Phi \) not accounted for in the calculation [20]. Most important of all, the calculated QWS bands are indeed centered at the BZ boundary of the step modulation.

Therefore, the alignment of QWS with the BZ boundary of the step modulation arises from the interplay between electronic coherence and interference in the corrugated film geometry. If either of them was not fulfilled, this phenomenon would not be observed. This is indeed consistent with experimental observations. Due to the lack of electron coherence, \( d \) band electrons in corrugated Ag films behave similarly as those in flat Ag(111) films, only shifted in emission direction by roughly the miscut angle (see Fig. 5.9). In vicinal metal substrates, e.g., Cu(443), the \( sp \) bulk bands, which have no interference effect, albeit a large coherence length, are also identical to those of the on-axis substrates, only angularly offset by the miscut [21].
5.6 Blazed Diffraction of Final State

The current model can easily explain the experimental observations (1) and (2), as discussed above. The experimental observation (3) is related with the change of photon energy. A possible way to understand it is to view the two sets of QWS as originating from different Brillouin zones, similar to the argument of SS on vicinal metal surface (Fig. 5.3). At lower (higher) photon energies, QWS between $G_{000}$ and $G_{111}$ ($G_{111}$ and $G_{222}$) was probed, respectively (Fig. 5.7). However, it is difficult to predict at which photon energy this shift of spectral weight would occur, due to the well-known “$k_\perp$ problem” in photoemission (see Chap. 2) [22]. In fact, the direct correspondence between the [111] direction and the center of spectral weight suggests that there could be a more straightforward explanation.

Photoemission involves the excitation of the cavity modes into a plane wave state in the vacuum. Each (111) facet on the surface of the corrugated film corresponds approximately to a constant-phase plane for the $j = -1$ modes (Eq. (5.4)). Upon photoexcitation, this phase relationship is preserved, and the outgoing photoelectron wave is only important within a narrow angular cone centered about $\Delta k_x = 0$, or the [111] direction, in accordance with Eq. (5.5). The diffraction condition (or conservation of the in-plane crystal momentum) must also be satisfied; for the photoelectrons, $k_x = -g/2 + ig$, where $i$ is an integer. Constrained by these two conditions, the excitation order $i$ depends on the photon energy, which is illustrated in Fig. 5.14. For corrugated Ag films, at low photon energies (11, 15, and 22 eV), $i = 0$, and a set of quantum well states centered at $k_x = -g/2$ is observed (Fig. 5.7). At high photon energies (50, 78, and 90 eV), $i = -1$, and a set of quantum well states centered at $k_x = -3g/2$ is observed. Physically, the dominant final states move through different surface zones in the extended zone scheme with increasing photon energies; a strong transition is observed when the reduced $k_x$ matches that of the initial states. In other words, QWS intensities will be maximized when they coincide with the [111] emission direction (Fig. 5.7). Because the Fraunhofer diffraction pattern has a finite width, the transition from $i = 0$ to $i = -1$ is not an abrupt process. Our model explains all of the essential features of the data, including the asymmetry in the emission pattern between the $+x$ and $-x$ directions.

Our interpretation in terms of the blazed diffraction of final state offers an easy and straightforward explanation for experimental observation (3). In addition, our explanation
indicates that the QWS set observed at higher photon energies should be nothing more than a replica of the set observed at lower photon energies. This is indeed verified by our data of Ag films on Si(557)-Au surface (Fig. 5.13(b)). The results show that the set at 78 eV is indeed centered at \( k_x = -3g/2 = -0.493 \text{ Å}^{-1} \) and is otherwise a replica of the set at 22 eV centered at \( k_x = -g/2 = -0.164 \text{ Å}^{-1} \). Similar behavior is also observed in Pb films (Fig. 5.11), although the photoemission intensity is dramatically modulated by the matrix element due to the complex band structure of Pb. These observations confirm that the two sets of subbands are derived from the same cavity modes, but are observed in different zones.

Note that the alignment between the center of spectral weight and the Si[111] emission direction is not very accurate (blue slanted lines in Fig. 5.7 and 5.11). It appears that the center of spectral weight is always slightly off the Si[111] emission direction and towards the optical normal. This slight offset might be attributed to the Nagai tilt of the film, as discussed in Sec. 5.3. For Ag films, the Ag[111] direction could actually be \( \sim 2^\circ \) off the Si[111] direction and towards the optical normal (Si[557] direction).

## 5.7 Conclusions and Outlook

Our results show that the electronic states in the corrugated Ag and Pb metal films are coherent and well-described by quantum well states bounded by parallel gratings. Their modulated electronic structures could give rise to useful transport and transmission properties suitable for device architecture in the quantum regime. Stepped surfaces with different step periodicities can be prepared by varying the miscut angle, and the film thickness can be controlled at the atomic level. These degrees of freedom allow for the preparation of corrugated films with tailored geometries suitable for applications.

There are a few interesting experiments that can be carried out in the future. For example, evidence of the Nagai tilt has been observed for corrugated Ag films from the photoemission spectra of \( d \) bands. Surface X-ray scattering experiments can help confirm this tilt and investigate the in-plane ordering of corrugated Ag films. In addition, other chain structures with a different corrugation periodicity, e.g., Si(553)-Au chains, can be used to grow corrugated metal films. It would be interesting to see whether quasi-1D electron system, e.g., stripes, can be created by employing substrates with smaller corrugation periodicity.
There is a great deal of theoretical work that remains to be done as well. For example, we modeled the electron reflection from a (111) terrace based on Fraunhofer diffraction, which assumes a mirror-like surface. The real surface consists of atoms arranged in an ordered array, so the reflection should be much more complex. Therefore, more realistic calculations that take into account the real atoms and the photoemission process are needed in order to thoroughly understand the photoemission spectra from these systems.

REFERENCES


FIGURES

Figure 5.1. Spin-charge separation in 1D electron gas [6]. (a) Schematic band dispersion characterizing a 1D electron gas in reciprocal space. Instead of a single band, one has two collective excitations (the holon and the spinon). (b) Real space visualization of the separation of a photohole into a holon and spinon. The propagation of holon and spinon is governed by two different processes (curved arrow), leading to different group velocities.

Figure 5.2. Band dispersion (c) and Fermi surface (b) of Si(553)-Au chain structure from ARPES [11]. The Brillouin zone is given in (a), together with a tight binding fit to the Fermi surface. $x (y)$ is the direction parallel (perpendicular) to the chain, respectively.
Figure 5.3. Left panel: Surface state dispersion perpendicular to the steps for Cu(443), measured with various photon energies, probing different wave vectors \( k_z \) normal to the surface between \( \mathbf{G}_{111} \) and \( \mathbf{G}_{222} \) [12]. The SSs are centered at the BZ boundaries of the step superlattice, marked by dashed lines, which indicates that the SS are coherent across the steps. The SSs arise from the partial energy gaps at L points. Right panel: Schematic diagram showing the origin of the SS alignment and the photon energy dependence [13]. The curves show the probed \( k \) space for various photon energies (arrow direction indicates higher photon energy) and the hatched regions represent the spread of the surface state wave function in \( k \) space.
Figure 5.4. Band dispersion of a 26 ML corrugated Ag film grown on a Si(111)-(4X1)-In surface measured along the direction parallel to the steps (a) and perpendicular to the steps (b) [14]. The spectrum shown is a second derivative of the experimental data.

Figure 5.5. (a) Schematic view of the corrugated film geometry and definition of coordinate systems in our experiment. (b) RHEED pattern of a 15 ML corrugated Ag film on Si(557)-Au surface. The measurement direction of RHEED pattern is indicated in the inset. The X5 periodicity along x direction is due to step modulation, while the X2 periodicity along the y direction originates from the Si(557)-Au substrate and is preserved after Ag film deposition.
Figure 5.6. Photoemission spectra of a 15 ML corrugated Ag film at various photon energies, recorded as a function of emission angles. The measurement direction is perpendicular to the steps (x direction). Vertical cyan lines and blue lines mark the optical normal (Si[557]) and Si[111] direction, respectively.
Figure 5.7. Photoemission spectra of a 15 ML corrugated Ag film at various photon energies, recorded as a function of the in-plane momentum $k_x$. Vertical green lines mark zone boundaries associated with the step modulation, and the blue slanted lines correspond to a fixed emission direction along the Si[111]. The faint vertical stripes in the spectra taken at 11 and 15 eV are artifacts caused by data stitching over different angular ranges; these artifacts are apparent only at low photon energy. The very sharp features right at the Fermi level are derived from the Ag(111) Shockley surface state.
Figure 5.8. Photoemission spectra of a 14 ML Ag film grown on Si(111) at various photon energies, measured along the $\Gamma\bar{M}'$ direction ([112]). The blue lines correspond to a fixed emission direction along the Si[111]. Only one set of QWS bands can be seen and is always aligned with the [111] direction.
Figure 5.9. Photoemission spectra of $d$ bands from a 14 ML Ag film on Si(111) (left) and a 15 ML corrugated Ag film on Si(557)-Au surface (right) at various photon energies, measured along the $\Gamma \overline{M}'$ direction. Left: $d$ bands are centered along the Si[111] direction (blue lines). Right: $d$ bands are approximately centered at -7.5 ° (vertical red lines) which is ~2° off the Si[111] direction (at -9.5°) towards the surface normal. Slanted green lines mark zone boundaries that are associated with step modulation.
Figure 5.10. Projected bulk band structure of a 9 ML Pb(111) film. Horizontal dashed line indicates the Fermi level.
Figure 5.11. Photoemission spectra of a 21 ML corrugated Pb film at various photon energies measured along the direction perpendicular to the steps. Vertical green lines mark zone boundaries that are associated with step modulation, and the blue slanted lines correspond to a fixed emission direction along the Si[111].
Figure 5.12. (a) Schematic view of the wave interference in corrugated films. (b) Diagram of momentum transfer as a result of diffraction from a single (111) terrace. (c) Fraunhofer single-slit diffraction pattern as a function of $\Delta k_t$. The red dots on the curve correspond to the diffraction with different $j$ values (Eq. (5.4)). Apparently, $j=-1$ is the only important one.
Figure 5.13. Calculated quantum well subband dispersion relations (green curves) compared with experimental results for a 15 ML corrugated Ag film. The experimental data have been processed by taking the second derivative along the energy axis to enhance the contrast. The photon energies used are 22 (a) and 78 eV (b).
Figure 5.14. Schematic view of the blazed diffraction of the final state. The direction of the outgoing photoelectron wave is constrained to near [111], due to the blazed condition of the final state. Diffraction from the step modulation gives rise to a momentum transfer of $ig$. These two constraints determine the photon energy dependence of the photoemission pattern.
6 Phonon-Induced Gaps in Graphite/Graphene

6.1 Introduction
ARPES is a powerful technique for determining the electronic structure of materials. It has been applied to numerous systems that are of scientific and technological interest [1]. Most studies of photoemission have focused on the spectral regions near the quasiparticle peaks, where the photoemission spectra are directly related to the quasiparticle self-energies [2]. Photoemission spectra far away from the quasiparticle peaks arise from higher-order electron scattering, including defect scattering and scatterings by elementary excitations, e.g., phonons. Although it has been speculated that this photoemission “background” carries information regarding electronic interaction with elementary excitations, there are significant difficulties in attempting to identify these interactions explicitly. A generic electronic state in a solid could scatter into many other electronic states as a result of coupling with elementary excitations. Therefore, the total contributions from all electronic states in a normal material would lead to enormous complexities in the photoemission background. Additional complications could arise due to the existence of defect scattering.

Our work on graphene systems shows that photoemission spectra away from the quasiparticle peaks provide another opportunity to study electron-phonon coupling. Unlike many other materials that have rather complicated Fermi surfaces, the Fermi surface of graphite/graphene consists of only six points at \( \mathbf{K} \) (\( \mathbf{K}' \)) points in the 2D Brillouin zone (see Sec. 6.2 for details). Careful experimentation with several graphitic materials, including highly oriented pyrolitic graphite (HOPG), natural single-crystal graphite (NSCG), and few-layer graphene systems (FLG) prepared on SiC(0001), allowed us to successfully identify the “intrinsic” photoemission spectra that arise from electron-phonon coupling. The hallmark of electron-phonon coupling in these materials is the gaps near the normal emission, which diminishes with increasing emission angles. Additional experimental evidences confirm that electron-phonon coupling is indeed the underlying mechanism.

Before examining the details of our own experiment, a brief introduction to graphite/graphene will be given in Sec. 6.2. In order to better illustrate the concept of phonon-
assisted photoemission, its physical picture will be presented first and the theoretical results will then be compared with the experimental data from HOPG (Sec. 6.3). Our experiments will be discussed in detail in Sec. 6.4 and 6.5. All of these results are consistent with the phonon-assisted photoemission mechanism. In order to verify that phonon scattering is the only plausible explanation for the observed gaps, consequences from other possible scattering processes will also be discussed (Sec. 6.6). The experiment data shows a dominant coupling with the out-of-plane phonons at the K point, which can be explained in terms of the parity selection rule (Sec. 6.7). Finally, our ARPES results will be compared with the STM measurements, which show very similar gaps in the tunneling spectrum (Sec. 6.8).

6.2 Graphene Age

Free-standing graphene was discovered only recently, long time after graphite, its parent, was discovered thousands years ago [3]. Single-crystal graphite is essentially a stack of graphene layers (AB stacking) weakly bonded together by van der Waals forces (Fig. 6.1). The weak bonding between graphene layers makes graphite extremely easy to cleave. For example, one can simply use a Scotch tape to peel off graphene layers and obtain a good cleave on graphite surface. In fact, this simple technique of cleaving graphite, which is known as graphite drawing, was used to discover free-standing single layer graphene [3].

The weak van der Waals bonding and the large interlayer spacing between graphene layers imply that graphite is essentially a quasi-2D crystal and should be very similar to graphene. Fig. 6.2 shows the electronic band structures and phonon dispersion relations for graphite and graphene obtained from first-principle calculations based on the ABINIT program [4,5,6,7]. These calculations were based on the local-density approximation (LDA), and yield a fairly good overall description of the experiment. The calculated results are quite similar for graphene and graphite within the basal plane. The dispersions for graphite are small along the z direction (perpendicular to the basal plane). For the sake of simplicity, the discussion in this chapter will mostly refer to the graphene dispersion relations. The difference between graphite and graphene will be mentioned whenever it is important.

The electronic structure of graphene (Fig. 6.2(b)) is straightforward to understand. Each carbon atom has four valence electrons, three of which hybridize (sp² hybridization) and form σ bonds with the three nearest neighbors. The remaining valence electron develops pₓ orbital and
forms π bonds with neighboring carbon atoms. The most striking feature of the π band is that it crosses the Fermi level at exactly the $K$ ($K'$) point and develops linear dispersion near this region. These linear bands are called “Dirac cones,” while the crossing point is termed as the “Dirac point.” This peculiar linear band dispersion indicates that the charge carriers (electrons or holes) near the Dirac point behave like Massless Dirac Fermions (band dispersion is generally parabolic near an extreme point as a result of an effective electron/hole mass).

Before we examine the physics of graphene that arises from this linear band dispersion, let us first understand how these Dirac cones are formed. It turns out that this linear band dispersion near $K$ ($K'$) point is a direct consequence of graphene’s lattice symmetry [8]. Its honeycomb lattice consists of two equivalent carbon sublattices $A$ and $B$. In the spirit of tight-binding approximations, the $p_z$ orbital from these two sublattices overlap and cosin-like energy bands associated with the sublattices intersect at zero energy near the edges of the Brillouin zone, giving rise to conical sections of the energy spectrum near the Fermi level (Fig. 6.3). Tight-binding calculation yields the following band dispersion relation [9]

$$E_z = \pm t \sqrt{3} + f(k) - t'f(k), \quad (6.1)$$

where

$$f(k) = 2\cos(\sqrt{3}k_ya) + 4\cos(\frac{\sqrt{3}}{2}k_ya)\cos(\frac{3}{2}k_xa), \quad (6.2)$$

t is the nearest-neighbor hopping energy (hopping between different sublattices), and $t'$ is the next nearest-neighbor hopping energy (hopping in the same sublattice). The plus(minus) sign in Eq. (6.1) applies to the π*(π) band, respectively. Since $t'$ is very small (~0.1 eV) [10], the dispersion near the $K$ point can be approximated as

$$E_z(q) = \pm v_F |q| + O((q/K)^3) \quad (6.3)$$

where $q = k - K$ is the momentum measured relative to the Dirac points and $v_F$ is the Fermi velocity, with a value $v_F \approx 1\times10^6$ m/s [10]. This conical band dispersion can be clearly seen in Fig. 6.3.

Mathematically, the band dispersion near the $K$ point can formally be described by the Dirac-like Hamiltonian

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} = \hbar v_F \sigma \cdot q, \quad (6.4)$$
where $\sigma$ is the 2D Pauli matrix. Eq. (6.4) indicates that the electrons (holes) in graphene exhibit constant group velocity $v_F$ and can be viewed as relativistic massless Fermions. The $k$-independent Fermi velocity $v_F$ plays the role of the speed of light. However, there are fundamental differences in the two-component wave function (spinor) between “real” massless Fermions and electrons in graphene. The spinor of “real” massless Fermions refers to particle spin index (spin up and down), whereas the spinor of electrons in graphene stands for the relative contributions in the make-up of quasiparticles from two different sublattices. In this reason, the spinor of electrons in graphene is generally called the pseudospin.

Massless Dirac Fermions in graphene manifest themselves in the anomalous half-integer quantum hall effect (QHE). The Quantum Hall effect is a quantum-mechanical version of the Hall effect [11]. For normal two-dimensional electron systems subject to low temperatures and strong magnetic fields, the Hall conductivity $\sigma_{xy}$ takes on the quantized values

$$\sigma_{xy} = v \frac{e^2}{h},$$

(6.5)

where $e$ is the elementary charge of electron and $h$ is Planck’s constant. The prefactor $v$ is known as the “filling factor,” and takes on integer values (we restrict this discussion to integer QHE). The quantization of the Hall conductivity is universal for 2D electron systems and is precisely determined by elementary physical constants ($e$ and $h$). The integer QHE is very well understood, and can be simply explained in terms of the Landau levels (LLs) formed in a magnetic field. The QHE in graphene is anomalous in the sense that prefactor $v$ is a half-integer [12,13]. The Hall conductivity $\sigma_{xy}$ in graphene can be written as

$$\sigma_{xy} = \pm 4(N + 1/2) \frac{e^2}{h},$$

(6.6)

where $N$ is the Landau level index. The sign of $\sigma_{xy}$ depends on the charge carrier type in the graphene device. If the charge carrier is electron (hole), i.e., the Fermi level is above (below) the Dirac point, $\sigma_{xy}$ is positive (negative). The charge carrier in graphene can be induced by applying a voltage to the gate (typically Si substrate) (Fig. 6.5). The factor 4 appears due to the double valley and double spin degeneracy. Fig. 6.4 shows this half-integer QHE in a gated graphene device.
This half-integer sequence in the filling factor provides critical evidence of massless Dirac Fermions in graphene. The quantization of graphene’s electronic spectrum in magnetic field $B$, as a result of its quantum electrodynamics (QED) description, is given by $[14,15]$

$$E_N = \pm \sqrt{2e\hbar v_F^2 |N| B},$$

(6.7)

where +(-) refers to electrons (holes). The existence of a quantized level at zero energy ($N=0$), which is shared by electrons and holes, gives rise to the extra 1/2 term in Eq. (6.6) $[16]$. This quantization is in sharp contrast with the ordinary Landau levels with

$$E_N = \frac{\hbar eB}{m} (N + \frac{1}{2}),$$

(6.8)

which results in a normal integer sequence described in Eq. (6.5). A more intuitive explanation for the half-integer QHE is to invoke the coupling between pseudospin and orbital motion. QED predicts that the spinor for massless Fermions will change its sign under a $360^\circ$ rotation, indicating a phase change of $\pi$, called a Berry’s phase $[9]$. Therefore this geometrical phase of $\pi$ accumulated along cyclotron trajectories under the magnetic field will give rise to a $\pi$-shift in the phase of quantum oscillations and, in the QHE limit, to a half-step shift.

Graphene thus exhibits electronic properties that are distinctive for a 2D gas of particles described by the Dirac equation rather than the Schrödinger equation. This opens up the new possibility of studying phenomena related to QED in a benchtop condensed-matter experiment. For example, one of the most exotic and counterintuitive consequences of QED is the so-called Klein paradox, which predicts unimpeded tunneling of relativistic particles through high and wide potential barriers. However, such an effect has never been observed in particle physics. It has been proposed that the test experiment is conceptually easy to implement in graphene $[17]$. In fact, there has been some recent experimental evidence that supports Klein tunneling in graphene devices $[18,19]$. As the gold rush for graphene continues, one might expect more exciting physics from this fascinating material.

Strictly speaking, only electrons in free-standing single layer graphene can be regarded as being massless Dirac Fermions. For example, electrons in two monolayer graphene (2 ML) show a very small deviation from the linear dispersion, which results in a finite mass of $\sim 0.05m_e$ near the K point. This finite mass is due to the small, yet existent, interlayer coupling. Nevertheless, the electrons can still be regarded as massive Dirac Fermions $[9]$. For graphene layers with higher thickness, or even single-crystal graphite, the $\pi$ band still exhibits striking linearity, as
verified by ARPES measurements [20]. We will discuss these ARPES measurements in more detail later. The key point here is that the π band mostly preserves its linearity despite the small interlayer coupling.

While physicists see graphene as the ideal toy for playing QED games, material scientists look forward to utilizing it for next generation high-power, higher-frequency electronic devices. This may be the reason why graphene has attracted such widespread interest. One exceptional feature of graphene is its pronounced ambipolar electric field effect, i.e., its charge carriers can be tuned continuously between electrons and holes in concentrations $n$ as high as $10^{13}$ cm$^{-2}$, simply by applying a gate voltage in a graphene field-effect device (see Fig. 6.5). At the same time, the mobilities of the charge carriers ($\mu$) remain high (exceeding 15,000 cm$^2$V$^{-1}$s$^{-1}$) even at the highest electric-field-induced concentrations, and seem to be little affected by chemical doping [3,12,13]. This translates into the ballistic transport of graphene on a submicrometer scale at 300 K. Ballistic transport, which is often mentioned in the transport of graphene and carbon nanotubes, refers to the transport of electrons with negligible electrical resistance due to scattering. Ballistic transport occurs when the mean free path of electrons is much larger than the confinement size of the electrons. A room-temperature ballistic transistor has long been a tantalizing, but elusive, aim of electronic engineers and graphene can make this happen.

Despite the potential applications of graphene in electronics, significant obstacles remain in graphene-based electronics. One major problem is that graphene remains metallic even at the neutrality point (Dirac point). Therefore, artificially creating a band gap at the Dirac point is a critical step towards graphene device applications. One way to open a gap is to break the symmetry of the two sublattices in single-layer graphene by growing the graphene on an incommensurate substrate, e.g., 6H-SiC [21]. A more suitable system for creating controllable band gap is bilayer graphene [22,23]. The idea is to break the symmetry of the two layers in bilayer graphene, either by means of the electric field effect [22] or chemical doping [23]. A recent study shows that a continuously tunable band gap of up to 250 meV can be achieved through a dual-gate bilayer graphene field-effect device [24].

It has been slightly more than six years since graphene was first reported, and remarkably rapid progress has already been made towards graphene-based electronics. The intrinsic transport properties of graphene are determined by electron-phonon coupling [25]. Therefore, an in-depth understanding of this fundamental interaction in graphene systems is critical for graphene device
design and architecture. Let us now focus on e-ph coupling in graphene/graphite and see what photoemission can reveal about e-ph coupling in these materials.

6.3 Phonon-Assisted Photoemission

Photoemission is very useful for studying e-ph coupling in solids, since it directly probes the spectral function of the quasiparticle (See Sec. 3.3). The spectral function, measured from APRES, can be expressed in terms of the complex self-energy $\Sigma(k, \omega)$ as

$$A(k, \omega) = \frac{|\text{Im} \Sigma(k, \omega)|}{(\omega - \omega_b(k) - \text{Re} \Sigma(k, \omega))^2 + (\text{Im} \Sigma(k, \omega))^2},$$

where $\omega$ is the energy, $k$ is the wave vector, and $\omega_b$ is the bare band dispersion in the absence of many-body effects. $\Sigma(k, \omega)$ contains both the scattering rate and the renormalization of the band dispersion in its imaginary and real parts, respectively. The characteristic signature of e-ph coupling in photoemission spectra is the “kink” of the quasiparticle band dispersion near the Fermi level, which is caused by sudden changes in $\Sigma_{e-ph}(k, \omega)$ (the self-energy arising from electron-phonon interaction) as the electron energy $\omega$ crosses $-\omega_{\text{phonon}}$ (zero is Fermi level).

An example of such a kink observed in graphite, is shown in Fig. 6.6 [20,26]. A clear deviation from the linear band can be observed at energy around -0.15 eV (150 meV below Fermi level). In addition, a sharpening of the quasiparticle peak occurs above -0.15 eV. The position of this “kink” is consistent with the typical phonon energies at the K point in graphene (Fig. 6.2), which suggests that e-ph coupling is the underlying mechanism. $\Sigma_{e-ph}(k, \omega)$ depends on the number of decay channels for the photohole through phonon emission (phonon absorption is quenched because measurements are carried out at low temperatures). For electrons far below the Fermi level, $\Sigma_{e-ph}(k, \omega)$ is a constant. This is the case because the number of decay channels is fixed by the phonon energy window. However, For electrons with energies $\omega > -\omega_{\text{phonon}}, \Sigma_{e-ph}(k, \omega)$ suddenly changes due to decreased number of decay channels for the photohole (electrons above the Fermi level are not occupied and therefore cannot contribute). This gives rise to a decreased phonon scattering rate and a renormalized band energy for electrons with energies $\omega > -\omega_{\text{phonon}},$ leading to the characteristic phonon “kink.” The magnitude of this kink depends on the e-ph coupling strength $\lambda$ (also called electron-phonon
mass enhancement parameter) [27]. In the case of graphite and graphene, e-ph coupling is very small \((\lambda \sim 0.15 - 0.3)\) [28,29] and therefore the “kink” is not very obvious.

This phonon “kink” is commonly used in the ARPES community to study e-ph coupling in 2D materials [30]. Fig. 6.7 shows another example of such an application on single-layer graphene grown on SiC wafers [29]. Assuming that the bare band dispersion \(\omega_b\) is linear, \(\Sigma_{e-ph}(k, \omega)\) can be extracted from the experimentally measured peak positions and widths (Fig. 6.7(d)). The resulting \(\Sigma_{e-ph}(k, \omega)\) exhibits a main feature at \(\omega = -150\) meV and a fine structure at \(-60\) meV, which were assigned to coupling with in-plane phonon modes and out-of-plane phonon modes at K point, respectively (see Fig. 6.8). Note that in this case the dominant coupling is with the in-plane phonon modes at the K point.

Before introducing the concept of phonon-assisted photoemission, we first briefly discuss the phonon modes in graphene, which we will encounter frequently below. The phonon dispersion relations of graphite (essentially the same as graphene) have been measured by inelastic neutron scattering (INS) and inelastic X-ray scattering (IXS) [31,32,33,34]. The experimental results (Fig. 6.8) are fairly consistent with the first-principle calculations shown in Fig. 6.2. The polarization of each vibration mode at K point is also shown in the lower panel of Fig. 6.8. Note that four phonon modes at the K point with energies clustered around 150 meV have in-plane polarizations and the remaining two degenerate phonon modes at energy 67 meV are polarized along \(z\).

Most of the previous ARPES studies of graphite and graphene have focused on the Dirac cone features near the K point, but the photoemission spectra near the Fermi level at the \(\Gamma\) point have never been studied. Based on the conventional wisdom, there is nothing to look at because no “real” electronic states exist in that region (see Fig. 6.2(b)). Fig. 6.9 shows a high-resolution scan at normal emission from HOPG taken at 22 eV [35]. HOPG is composed of graphite crystallites highly oriented, within 0.4°, along the \(c\) axis, but the in-plane orientation of the crystallites is completely random. The typical crystallite size is 1 to 10 µm in the basal plan and >0.1 µm perpendicular to the basal plan [36]. Note that the normal emission spectrum is not affected by the rotational disorder due to the good orientation of crystallites along the \(c\) axis. The most striking feature in the spectrum is a pronounced gap of around 67 meV, which is accompanied by a weak gap of 150 meV and a residual Fermi edge.
Although direct emission from the quasiparticles is forbidden near the Fermi level at the \( \Gamma \) point, indirect emission through coupling to phonons is still allowed. In fact, the sizes of the gaps are consistent with the typical phonon energies in graphite (Fig. 6.2 and Fig. 6.8), implying that its origin is phonon coupling. Quite a few follow-up experiments have been carried out to confirm this origin and exclude other possibilities which might give rise to these gap features. Before going into these follow-up experiments, we will first discuss how this phonon-assisted photoemission occurs.

Due to energy conservation, the emission near the Fermi level at \( \Gamma \) point must arise from the electrons at the Dirac cones near the K point. Momentum conservation for normal emission from these states requires the involvement of a phonon near the K point. Given that the measurement temperature (60 K) is significantly lower than the Debye temperature of graphite, phonon absorption is quenched and only phonon emission contributes to this process. Therefore, the electrons at normal emission originate from the emission of electrons at the Dirac cones through the emission of a phonon near K point. The resulting normal emission spectrum should exhibit gaps below the Fermi level, whose sizes correspond to phonon energies at the K point. In the current case, the dominant gap (67 meV) arises from coupling with out-of-plane phonons at the K point (Fig. 6.8), while the weak gap at -150 meV comes from coupling with in-plane phonons. The dominance of coupling with out-of-plane phonons is due to a parity selection rule, which we will discuss in detail in Sec. 6.7.

At finite temperatures, the normal emission spectra for graphite can be approximated by

\[
I(E) \propto \sum_j A_j |E_D - E_j - E| F(E - E_F + E_j; T)
+ \exp \left( \frac{-E_j}{k_B T} \right) |E_D + E_j - E| F(E - E_F - E_j; T),
\]

(6.10)

where \( E_D, E_j, E_F, E \) are the Dirac point energy, the energy of the phonon with branch index \( j \), the Fermi level, and the electron energy, respectively. \( F \) is the Fermi-Dirac distribution function, and the factor \( \exp \left( \frac{-E_j}{k_B T} \right) \) is the branching ratio between phonon absorption and emission processes. The density of states is assumed to be linear (with zero at the Dirac point), and the product of photoemission cross section and electron-phonon coupling strength for each phonon branch, \( A_j \), is taken to be a constant. Strictly speaking, the phonon energy \( E_j \) is a function of the electron energy \( E \) due to the involvement of phonons with different momenta (see Fig. 6.10).
However, because the change of phonon energy as a function of momentum is much smaller than is the case for electron, Eq. (6.10) should be valid provided that we are only dealing with emission near the Fermi level. The green curve in Fig. 6.9(a) is a fit to the experimental data at temperature $T=60$ K, assuming two phonon modes and a metallic Fermi edge due to defect scattering (see Sec. 6.4). The fit, which shows excellent agreement with the experimental data, yields $E_j=64$ meV and 153 meV, consistent with the phonon energies at the K point. The position of the Dirac point, obtained from the fit, is at $\sim 0.1$ eV above the Fermi level, which is in reasonable agreement with the Dirac cone measurement (see Fig. 6.11(a)). Although the theoretical Dirac point for bulk graphite or free-standing graphene should be exactly at the Fermi level [8], the experimental Dirac point for either bulk graphite or freestanding graphene appears to always be slightly above the Fermi level (for example, see [3,20]). It was suggested that this shift of Fermi level might be caused by residual water on the graphite/graphene [3].

At higher temperatures, phonon absorption processes could fill in the gap. However, with $E_j/k_B=770$ K (for out-of-plane phonons at K point), the gap remains visible even at room temperature. This is indeed confirmed by the experiment (Fig. 6.11(b)). The spectrum at 300 K is very close to that at 60 K, except from a thermally broaden gap edge, which indicates that e-ph coupling strength is essentially unchanged from 60 K to 300 K because the phonon absorption is still quenched in this temperature region. This is consistent with a previous ARPES measurement which shows almost temperature-independent e-p coupling for graphite up to 200 K [37].

Although our proposed phonon-assisted photoemission can explain the experimental results from HOPG, further evidences are needed to exclude other possible mechanisms and to confirm that its origin is e-ph coupling. After all, the emission features observed in our experiment are weak (within the band gap) and other scattering processes, e.g., defect scattering, might be significantly affecting the normal emission spectra. The following two sections provide more experimental evidences that support the interpretation of phonon-assisted photoemission.

### 6.4 Universal Gaps in Graphitic Materials

In order to verify the nature of the observed gaps in HOPG, further experiments were carried out on natural single-crystal graphite (NSCG) and few-layer graphene systems (FLG) prepared on SiC(0001). We observed similar gap features in all these systems, suggesting that the gap features at normal emission are universal in graphitic materials.
Before continuing with the discussion of the experimental results, we briefly summarize our experimental methods here as a reference. The HOPG and NSCG samples, mounted on Si(111) substrates, were cleaved using sticky tapes, transferred immediately into the measurement chamber, and were then annealed at 650 °C for several hours by passing a current through the Si substrate. The Si-terminated SiC(0001) sample, of the 6H polymorph, was cleaned in the air by exposure to ozone generated by an ultraviolet lamp. Once transferred into the measurement chamber, it was outgassed by passing a current through the sample itself. Various surface reconstructions and graphene layer configurations were prepared by high temperature treatment and were characterized by reflection high energy electron diffraction. Our ARPES measurements were performed using the PGM-A, U-NIM, and Wadsworth beamlines at SRC. The energy and momentum resolutions were 20 meV and 0.01 Å⁻¹, respectively. All spectra were taken with the sample temperature at 60 K, unless otherwise stated.

HOPG can, upon cleavage, yield an inhomogeneous surface with varying densities of defects including steps. It is important to ascertain the sample quality within the spot of illumination during the photoemission measurements. For each cleave in our experiment, survey ARPES spectra were taken at different positions on the surface. The results were generally consistent, but with different levels of background emission and sharpness of the primary ARPES features. Much worse spots could be found occasionally. The results are explained in terms of scattering by defects of the primary electrons leading to a secondary electron background and smearing of the primary ARPES features. As an example, Fig. 6.12 shows normal emission spectra obtained at four different spots, P1-P4, on one HOPG sample, using 22 and 26 eV photons [38]. Through experimentation with a larger number of samples and spots, we conclude that spectra like those from P1 and P2 are about the best that can be obtained and must be close to being intrinsic for HOPG. Emission from the gap region at normal emission (Fig. 6.12(c)) indicates that there is a correlation between the intensity of the background emission and the height of the Fermi edge in each case. The step height associated with the gap remains the same for the cases P1-P3. For P4, the gap is no longer apparent due to the high background emission. Due to the small crystallite sizes in HOPG, some defect emission is inevitable. This might explain the residual Fermi edge in the best spectra.

The result from NSCG is almost identical to that of HOPG. The normal emission spectrum of NSCG, shown in Fig. 6.13(a), exhibits an apparent gap of ~67 meV and a weak gap of ~150
meV. The gap features are not as sharp as HOPG, because there is a somewhat higher background in the gaps, which is likely caused by impurities and defects in natural crystals. Fig. 6.13(a) also shows the symmetrized spectrum with respect to the Fermi level. The symmetrization is accomplished by adding each spectrum to its mirror image about the Fermi level (Fig. 6.13(b)). This symmetrization procedure has been employed by others to analyze the superconducting gap in high-temperature superconductors (see, for example, [39]). The results highlight gap features near the Fermi level, and mimic what one might observe with scanning tunneling spectroscopy (STM). In the present case, symmetrization removes the Fermi edge derived from impurity and defect scattering. This procedure is particularly helpful when impurity and defect scattering is intense.

The situation with FLG prepared on SiC(0001) is more complicated than that of HOPG and NSCG, due to the variation of the film thickness and the substrate effect. Graphene layers with various thickness can be obtained by carefully controlling the annealing temperature and time [23,40]. The thickness of the graphene layers are deduced through ARPES by the Dirac cone features, which are shown in Fig. 6.14(a). The number of split π bands corresponds to the number of graphene layers, which is similar to quantum well states in metallic films [41]. Note that the Dirac point is below the Fermi level, indicating that the graphene layers are doped (n-doped) as a result of contact with the SiC substrate. The Dirac point gradually approaches the Fermi level as the film thickness increases, which is in line with the upward shift of the σ band at normal emission (Fig. 6.14(b)) [21,40].

The normal emission spectrum near the Fermi level for 1 ML graphene is dramatically different from what one might expect based on phonon-assisted photoemission (Fig. 6.15(a)). This discrepancy can be attributed to the intensity contribution from the buried $6\sqrt{3} \times 6\sqrt{3}$ interface beneath the graphene layer. The $6\sqrt{3} \times 6\sqrt{3}$ interface, which is very likely to be one layer of graphene whose pz orbital hybridizes with the substrate, has a broad surface state at around -0.6 eV [42]. Because the electron escape depth for the current case (kinetic energy of electron is about 45 eV) is 5~10 Å [43], spectral contribution from the $6\sqrt{3} \times 6\sqrt{3}$ interface could be significant at low graphene coverages. As the graphene layers become thicker, the contribution from the interface is expected to decrease exponentially, which is verified by the
measurement of Si 2p core level (Fig. 6.15(b)). At 2 ML already, the Si 2p signal almost disappears and a gap of ~67 meV shows up at the Fermi level.

Fig. 6.16 shows the phonon-induced gaps at normal emission for 3 ML and 4 ML graphene. For a better illustration of the gaps, the symmetrized spectra are also presented. The gap at -67 meV can be clearly seen in both coverages. However both cases reveal an obvious metallic Fermi edge, which is considerably larger than that of HOPG and NSCG. This large metallic Fermi edge arises from the small domain sizes (30-200 nm) of the epitaxial graphene layers, which give rises to enhanced defect scattering [44]. As a result, the expected gap at -150 meV is no longer observable.

The gap feature in 4 ML is somewhat weaker than 3 ML, which is caused by increased roughness at higher graphene coverages. Epitaxial graphene layers on SiC(0001) are produced by heating the SiC sample to evaporate away the Si atoms near the surface. This high-temperature treatment inevitably gives rise to appreciable surface roughening beyond 3 ML [23]. Indeed, normal emission spectra (Fig. 6.14(b)) of graphene layers at various thicknesses show that the peak at about -4.3 eV derived from the σ band becomes less pronounced beyond 3 ML, suggesting increased surface roughness. For graphene layers thicker than 5 ML, the π bands near the K point become very broad (Fig. 6.17(a)). The increased roughness results in a less obvious gap (Fig. 6.17(b)). Nevertheless, the absolute first derivative of the spectrum (Fig. 6.17(b)) shows a clear peak at around -67 meV, confirming the existence of the gap. The filling in of the gap can be attributed to defect scattering that smears out the phonon spectrum. An equivalent view is that momentum conservation is no longer strictly obeyed, and phonons away from the K point in the Brillouin zone can also contribute to phonon-assisted photoemission at normal emission.

The fact that similar gap features exist in all three systems suggests that these gaps are intrinsic spectral features of graphitic materials. Experimental observations also indicate that defect scattering gives rise to a featureless background emission and a residual Fermi edge. This is consistent with a previous theoretical study, which shows that defects such as point defects can result in enhanced density of states near the Fermi level [45]. Therefore, the consistency obtained from three systems provides further support for our interpretation. The next step is to utilize the unique advantages of ARPES and probe the angular and photon energy dependence of the gaps.
6.5 Angular and Photon Energy Dependence

The unique advantage of angular resolution in ARPES allows us to probe the angular dependence of the gaps. The best system for studying the angular dependence is epitaxial graphene layers prepared on 6H-SiC, due to its good in-plane orientation. Fig. 6.18(a) shows the symmetrized spectra of 3 ML graphene as a function of in-plane momentum along the $\Gamma K$ direction. In order to better illustrate the gap, the corresponding first derivatives of the symmetrized spectra are also presented (Fig. 6.18(b)), which should exhibit peaks at the edges of the gaps. Apparently, the gap gradually diminishes and gets filled in for increasing in-plane momentum. This occurs because phonons at lower wave vectors (due to momentum conservation), and lower energies, become involved.

In order to demonstrate which phonons are actually involved in this process, Fig. 6.19 shows the available phonon-assisted photoemission channels for emission at an arbitrary in-plane momentum along the $\Gamma K$ direction. Due to the lattice symmetry, there are always two inequivalent phonon momenta involved. This could explain why we have not been able to resolve individual phonon gap at an arbitrary in-plane momentum (Fig. 6.18). However, if one were to measure the gap along the $\Gamma M$ direction, the gap should directly follow the phonon dispersion relation along the $\Gamma M$ direction since $q_1$ and $q_2$ would be identical. This suggests that the phonon dispersion relation along $\Gamma M$ could be obtained directly through this method, given that the energy resolution is good enough. At present we do not have data along the $\Gamma M$ direction, but this will certainly be an interesting experiment to carry out in the future.

Another advantage of synchrotron-based photoemission is the ability to vary the photon energy, which gives information about the dispersion along the $z$ direction (see Chap. 2). As discussed in Sec. 6.2, the dispersion along the $z$ direction for graphitic materials is small, and therefore the gap features are expected to be independent of photon energies. Fig. 6.20 shows normal emission spectra of HOPG taken at various photon energies. As expected, the main gap of 67 meV is essentially unchanged at different photon energies. The gap of 150 meV is not resolved in these photon energies, due to poorer energy resolution.

6.6 Other Scattering Processes
All of the current experiment observations are quite consistent with our interpretation of phonon-assisted photoemission. Indeed, e-ph coupling is the most natural explanation for experimental observations including the size of gaps, temperature dependence, angular dependence, etc. However, in order to verify that e-ph coupling is the only plausible explanation, we must investigate other possible scattering processes and determine whether they could give rise to the observed gap features. The scattering processes that are known to exist in graphite/graphene are defect scattering, electron-electron scattering, electron-plasmon scattering [28,37].

Defect scattering generally gives rise to a featureless background emission. This is consistent with our experimental results from three graphitic materials, which show that defect scattering leads to an enhanced background and a residual Fermi edge. Furthermore, it is unlikely that defect scattering could give rise to an angularly dependent gap. Electron-electron scattering should not yield any gap feature at all, because the scattering rate, according to standard Fermi-liquid theory, is proportional to $E^2$ with no abrupt onset [46]. A previous study even suggested that the electron-electron scattering in graphite is almost negligible due to lack of scattering phase space [37].

On the other hand, electron-plasmon scattering could give rise to a gap in normal emission through emission of plasmons and the gap size would be the plasmon energy at momentum $q=K$. Ordinary two-dimensional plasmons have a dispersion relationship

$$\omega_{pl}(q) = \sqrt{4\pi n e^2 q / m(1+\varepsilon)},$$

where $e$ is the electron charge, $m$ is the effective carrier mass and $\varepsilon$ is the dielectric constant. Because $m$ is very close to zero, the plasmon energy at $q=K$ is typically ~0.6 eV, as confirmed by ARPES and Electron-energy-loss spectroscopy (EELS) [28,47,48]. This value is one magnitude larger than the experimentally observed gap size. Furthermore, $m$ depends on the layer thickness for FLG prepared on SiC, and therefore the plasmon gap would be thickness-dependent, which is inconsistent with our experimental observations. We thus conclude that electron-plasmon coupling cannot be the underlying mechanism for the observed gaps. This leaves electron-phonon coupling as the only plausible explanation.

6.7 Selection Rule
Although phonon-assisted photoemission can explain our experimental results well, one question remains: why is the gap at -150 meV much weaker than the gap at -67 meV (see, for example, Fig. 6.9)? The answer is simply that the e-ph coupling matrix element for in-plane phonons is close to zero at normal emission due to wave function symmetries. Note that the gap at -150 meV is caused by in-plane phonons at K point (K2, K5, K1 modes, See Fig. 6.8) and the gap at -67 meV arises from out-of-plane phonons at K point (doubly degenerate K6 modes).

The initial state at the K point for graphene is

$$\psi_K(r) \propto \sum_{R} \phi(r - R) \exp(iK \cdot R), \quad (6.12)$$

where $\phi(r)$ is a carbon $p_z$ orbital, $K$ is the wave vector at the K point, and the summation is over all lattice vectors $R$. The orbital $\phi(r)$ is of even parity within the basal plane. There are actually two degenerate states; the other one involves a $p_z$ orbital centered about the other atom within the unit cell. Photoexcitation of this state leads to

$$\psi'_{K}(r) \propto \sum_{R} \phi'(r - R) \exp(iK \cdot R), \quad (6.13)$$

where $\phi'$ is an excited Wannier function. The excitation involves the usual dipole transition term $A \cdot P$ and a "surface transition" term arising from a non-zero $\nabla \cdot A$, where $A$ is the vector potential (see Sec. 2.5.2) [49,50]. Both terms are important for three-dimensional systems, but only the dipole term preserves the crystal momentum along $z$. Graphite is a quasi-two-dimensional crystal with a large perpendicular lattice constant $c = 6.7 \, \text{Å}$ compared with the $z$ extent of the $p_z$ orbital $\phi(r)$ of about $a = 1.4 \, \text{Å}$; the dipole term, $\left| \langle \phi' | A \cdot P | \phi \rangle \right|^2$, is scaled down by a factor of $\sim (a/c)^2$. On the other hand, the vector potential $A$ is close to the $z$ direction in the current experimental geometry, and therefore the surface transition term, which is proportional to $(\varepsilon - 1) A_z$, is not affected. As a result, surface transition dominates. Since this involves a $z$-dependent interaction, the in-plane parity of the state is preserved. Thus, $\phi'$ is also of even parity within the basal plane.

The state $\psi'_{K}$ can couple via a phonon of wave vector $-K$ to a state at the zone center:

$$\psi'_0(r) \propto \sum_{R} \phi'(r - R), \quad (6.14)$$
where $\phi''$ is another excited Wannier function. This state can couple to a plane wave in vacuum, and lead to normal emission, if $\phi''$ is of even parity within the basal plane [51]. Within the usual rigid-ion approximation (see Sec. 3.3.1), the electron-phonon coupling is

$$\Delta H \propto Q \langle \phi''(r) | e \cdot \nabla V(r) | \phi'(r) \rangle,$$

(6.15)

where $V$ is the ionic potential, $e$ is the phonon polarization vector, and $Q$ is the phonon normal mode coordinate. Because both $\phi'$ and $\phi''$ are of even parity within the basal plane, only phonons polarized along $z$ can contribute to this process.

Therefore, this parity selection rule that “forbids” coupling through in-plane phonon originates from the dominance of the surface transition term. The dipole transition term, even though suppressed, is nonzero, and its parity permits the excitation of the in-plane phonons. This is why a weak gap at -150 meV, corresponding to the in-plane phonons, can still be seen in HOPG and NSCG (Fig. 6.9 and 6.13). The gap should actually consist of three closely spaced gaps which correspond to the K2, K5 (doubly degenerate), and K1 modes at approximately 124, 151, and 164 meV, respectively (see Fig. 6.8), but we have been unable to resolve them due to limited energy resolution. This weak gap cannot be observed in FLG prepared on SiC due to enhance defect scattering.

The dominance of the surface transition is partially determined by the current experimental geometry. If one changed the polarization of the photon to make $A_Z$ zero, the surface transition term would become zero. In that case, there would be no parity selection rule and all of the phonons were expected to contribute equally. This would allow us to directly determine the energy for each phonon branch. We are looking forward to carrying out this experiment on the new variable polarization PGM beamline at SRC.

### 6.8 Gaps from STM Measurements

Interestingly, a similar gap was reported in a scanning tunneling spectroscopy (STM) study of graphene from a Berkeley group [52,53]. Fig. 6.21(a) shows a typical $dI/dV$ curve taken on a gated graphene flake device, which exhibits a gap of ±64 meV, very similar to our ARPES measurement (Fig. 6.21(b)). The gap is determined to be independent of the graphene layer thickness, the supporting substrates and charge carrier concentrations [52,53]. Due to the lack of DOS near the Fermi level close to $\Gamma$ point, the tunneling can only take place through the phonon-
assisted process. As a result, the gap was attributed to phonon-mediated inelastic tunneling [54], which is similar to the phonon-assisted process in photoemission. A recently published paper from the same group shows that a gap of ±150 meV, caused by in-plane phonon coupling, can be also observed through $d^2I/dV^2$ measurements [55].

However, there have been disagreements about the gap size or even the existence of gaps in previous STM studies [56,57,58,59]. The inconsistencies remain controversial and could be related to sample inhomogeneity, tip structure, or tunneling at the buried interface. In fact, the Berkeley group showed that the gap features are quite sensitive to tip damages and are easily distorted if the tip is slightly contaminated or damaged [53]. ARPES is free of tip effects, and therefore our result provides direct evidence of this e-ph coupling process. The mechanism leading to the ARPES gaps does not apply directly to the tunneling case. However, for a well collimated tunneling current perpendicular to the graphene layers from a tip with a simple density of states, same phonon emission processes will take place and identical gap features can be expected.

It is well known that ARPES and STM are two complementary techniques (reciprocal space vs. real space) and involve very different physical processes (photoexcitation vs. tunneling). The striking similarity between ARPES results and STM measurements in graphane/graphite suggests that the underlying electron-phonon interaction is an intrinsic and elementary interaction for these graphitic materials.

### 6.9 Conclusions and Outlook

The present study demonstrates that ARPES spectral regions forbidden for direct emission provide a valuable test ground for detailed investigations of elementary interactions. Electron-phonon coupling is a weak interaction, but its signature shows up clearly because of the absence of other spectral features. This insight is important for a detailed understanding of the basic physics of graphite and graphene. Possible applications of the method include phonon spectroscopy and determination of the electron-phonon coupling strength through a detailed analysis of ARPES data. More specifically, the phonon gaps at general points in the Brillouin zone could be used to extract detailed phonon dispersion relations, while the spectral height of each phonon gap provides a direct measure of the electron-phonon coupling strength.
Strictly speaking, the e-ph coupling leading to the gaps occurs in the final state, and is therefore a final state property (see Sec. 6.7). By contrast, the e-ph coupling which causes the “kinks” of the quasiparticle bands is an initial state property (Sec. 6.3). The “kinks” of the $\pi$ bands in graphene are primarily from in-plane phonons (150 meV) at K point (Fig. 6.7), which couples electrons at K point to K’ point (intervalley scattering). The gaps at normal emission are caused by the coupling of photoexcitated electron states to final states at $\Gamma$ point, and the dominant phonons are out-of-plane phonons at K point, as required by the parity selection rule.

These phonon-induced gaps should be observable for other materials which have simple, symmetric Fermi surfaces. A good candidate for observing these phonon-induced gaps will be the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface. The Fermi surface of this structure consists of small pockets (surface state) at the $\Gamma$ point of the superlattice [60]. There are no other occupied states near the Fermi level, due to the Si substrate. Other systems with a circle-like Fermi surface should also exhibit phonon-induced gaps at the $\Gamma$ point, if there is a “read” band gap near the Fermi level at the $\Gamma$ point.

REFERENCES


Figure 6.1. Crystal structure (left) and Brillouin zone (right) of graphite. The dashed lines on the left panel mark the unit cell of graphite. Graphite has a hexagonal crystal structure with four atoms per unit cell. On the other hand, graphene is a honeycomb lattice with two atoms per unit cell.
Figure 6.2. Band structures and phonon dispersion relations of graphite (a,c) and graphene (b,d) from first-principles calculations. The inset in (a) shows the two-dimensional Fermi surface of graphite and graphene, which consists of 6 Dirac points at $\bar{K}$ and $\bar{K}'$.

Figure 6.3. A 3D view of the band structure of graphene from tight-binding calculations [9].
Figure 6.4. Half-integer QHE in a gated graphene device [13]. Hall resistance $R_{xy}$ (black curves) for an electron gas (positively gated) shows characteristic plateaux in the strong magnetic field, corresponding to the regions of zero magneto-resistance $R_{xx}$ (red curves). The inset shows similar results from a hole gas (negatively gated).

Figure 6.5. Ambipolar electric field effect in single-layer graphene [3,16]. Left: schematic view of a typical graphene field-effect device. A voltage of $V_g$ is applied to the Si substrate (gate) to induce charge carriers in graphene. Right: the resistance of the graphene as a function of $V_g$. The insets show their conical low-energy spectra, indicating changes in the position of the Fermi energy $E_F$ with varying gate voltage $V_g$. The rapid decrease in resistivity with increasing charge carriers indicates their high mobility.
Figure 6.6. Photoemission spectra of graphite. Left: Spectra of graphite near the H point, measured along the direction perpendicular to the AH direction [20]. The Dirac cone-like π band can be clearly observed. Right: Zoom-in view of the π band near the Fermi level [26]. The arrow indicates the position of the phonon “kink” in the band dispersion.

Figure 6.7. Phonon “kink” in graphene [29]. (a) ARPES spectra near the K point. The “kink” position is highlighted by an arrow. (b) Comparison between experimental band dispersion relation (red curve) and theoretical linear band dispersion (gray dotted line). (c,d) Group velocity (c) and real part of the self-energy (d) as a function of energy deduced from dispersion plotted in (b). The inset in (d) shows the band width in momentum space as a function of energy, which is presumably proportional to the imaginary part of the self-energy.
Figure 6.8. Phonon dispersion relation of graphite, adapted from [33]. Solid lines are the force-constant calculations from the fifth-nearest neighbor fit and symbols are the experimental results from INS and IXS. The lower panel shows the eigenmodes at the K point (red arrows indicate the vibration direction of atoms).
Figure 6.9. Normal-emission spectrum from HOPG showing gaps induced by out-of-plane and in-plane phonons. (a) Integrated normal-emission spectra taken from multiple scans. The red line is a linear fit to the data at energies below $-0.25$ eV, and the green curve is a model fit assuming two gaps. The vertical dash lines indicate positions of the Fermi level and the edges of two gaps. (b) A zoom-in view of the spectrum near the gap edges. (c) Absolute value of the first derivative of (b). The zero level for each spectrum is indicated by a tick mark on the right vertical axis.
Figure 6.10. A schematic diagram that shows the normal emission spectrum arising from phonon-assisted photoemission process. Electrons at the Dirac cone emit phonons with specific momenta and contribute to the normal emission. The energy conservation gives rise to gaps in the normal emission spectrum.

Figure 6.11. (a) Measured dispersion of HOPG near $\bar{K}$ along a radial direction pointed away from $\bar{\Gamma}$. A quasi-Dirac cone can be seen and its Dirac point is at ~ 60 meV above the Fermi level, which was deduced by extrapolation of the linear bands. (b) Temperature dependence of the phonon-induced gaps at normal emission for HOPG. The blue dots are experimental results and the red curves are fit using Eq. (6. 10). The cyan dots are reference spectrum from Polycrystal Ag, which is in electrical contact with HOPG and serves as a reference for the Fermi level. The vertical dash lines indicate positions of the Fermi level and the edges of two gaps. The gap at -150 meV is no longer visible at 300 K, due to thermal broadening.
Figure 6.12. Position dependent normal emission spectra from HOPG. (a) Normal emission spectra of HOPG taken at 22 eV from four different spots, P1-P4, on the same sample. (b) Similar data taken at 26 eV. The red vertical dash line marks the band edge of graphite. (c) Detailed view near the Fermi level of the spectra taken at 22 eV. Spectra in (c) have been shifted vertically for clarity.
Figure 6.13. (a) Normal emission spectrum of NSCG and its symmetrized spectrum with respect to the Fermi level (labeled S). The cyan dot is a reference spectrum from Ag. (b) Symmetrization of the Fermi-Dirac function $F(E)$ for an assumed temperature of 60 K. The result is a horizontal line. Zero energy corresponds to the Fermi level.
Figure 6.14. Characterizing the thickness of graphene layers on 6H-SiC through ARPES. (a) Evolution of the Dirac-cone features near the $\bar{K}$ point as a function of layer thickness, measured along a direction perpendicular to $\bar{\Gamma}\bar{K}$. (b) Evolution of normal emission spectra. The peaks at around -4.3 eV and -8 eV are derived from the $\sigma$ band and the $\pi$ band, respectively. The photon energy used is 50 eV.
Figure 6.15. (a) Normal emission spectra near the Fermi level, as a function of graphene layer thickness. The broad peak at around -0.6 eV is from the $6\sqrt{3} \times 6\sqrt{3}$ interface. (b) Evolution of Si 2p core level as a function of graphene layer thickness.

Figure 6.16. Normal emission spectra and symmetrized versions (labeled S) for 3 and 4 ML graphene layers. Also shown for purposes of comparison is a spectrum near the K point for 3 ML, which shows no gap. The vertical dash lines indicate the positions of the Fermi level and the edge of the gap at -67 meV.
Figure 6.17. Gap in epitaxial graphene layers beyond 5 ML. (a) The π band near the $\overline{K}$ point for the surface with >5 ML graphene. The measurement direction is perpendicular to $\Gamma K$. (b) A normal emission spectrum, its symmetrized version, and the absolute value of its first derivative (FD) for the surface with >5 ML graphene.

Figure 6.18. Dependence of the gap on $k$. (a) Symmetrized spectra for 3 ML graphene as a function of in-plane momentum $k$ along the $\Gamma \overline{K}$ direction. (b) Absolute value of the first derivative of (a). The two vertical lines indicate the edges of the gap at normal emission.
Figure 6.19. Schematic diagram showing the available phonon-assisted photoemission channels at an arbitrary in-plane momentum along the $\Gamma K$ direction. (a) Electrons at the six Dirac cones can contribute through the emission of phonons with momentum $q_1$ to $q_6$. (b) The phonon momenta are folded back into the first BZ and only two phonon momenta are actually inequivalent due to lattice symmetry.

Figure 6.20. Photon energy dependence of the gaps at normal emission in HOPG.
Figure 6.21. Similarity of gaps observed in tunneling spectra of Graphene (a) and gaps in photoemission spectra of graphene/graphite (b). (a) was taken on a graphene flake device [53]. (b) is the symmetrized normal emission spectrum of HOPG.
7 Conclusions and Outlook

This dissertation reports ARPES studies of ultrathin metallic films and graphene systems, both of which have attracted considerable interest because of their technological importance, as well as their rich physics. Our study of ultrathin metal films show that the substrate lattice can cause diffractions at the interface and leads to additional interference effects in the QWS. In the case of Ag films on Ge(111), the incommensurate interface potential induces mixing of electron waves and gives rise to coherent electronic interference structures. Strictly speaking, the incommensurate interface breaks the translational symmetry of the film, but the photoemission patterns can still be explained by intermixings of QWS by the interface potential. For Ag and Pb films grown the Si(557)-Au surface, the highly stepped substrate results in formation of corrugated films, whose boundaries differ dramatically from their counterparts in uniform flat films. The corrugate film can be viewed as a one-dimensional cavity (along the z direction) bounded by two parallel gratings, and the interference of QWS consists of two conjugate umklapp diffractions at the surface and interface. These diffraction gratings are strongly blazed, which places a strong limit to the available diffraction orders.

Our work on graphene systems shows a new fingerprint of electron-phonon coupling in photoemission, namely, phonon-induced gaps in the spectral regions far away from the direct transition. Normally, photoemission intensity in this forbidden region is considered to be a background and therefore ignored. The signal from the electron-phonon coupling is very weak, and our success on graphene systems benefits from the large band gap at the Γ point and its point-like Fermi surface. The gaps observed at the normal emission are similar to those seen in the tunneling spectra from STM, thus confirming that this electron-phonon coupling is an intrinsic interaction in graphitic materials. The conclusion is that electronic coupling with out-of-plane phonons at the K point plays an important role in the tunneling and transmission properties of graphene devices.

The research in this dissertation can lead to a few research directions in the future. Some are particularly interesting and therefore deserve to be mentioned here. Our results in corrugated Ag and Pb films grown on the Si(557)-Au surface demonstrate that the QWSs are 2D and are coherent across the steps. It would be interesting to see the influence of the corrugation
periodicity on the QWS. The corrugation periodicity can be changed by varying the miscut angle of the Si(111) substrate. When the corrugation periodicity becomes sufficiently small, the stacking fault within the corrugated film might give rise to electronic localization perpendicular to the steps. Intuitively, this electronic localization could be more pronounced at small film thickness. The whole idea is to systematically examine the electronic structure of corrugated films as a function of both the corrugation periodicity and film thickness. As the experimental endeavor for 1D electron system continues, corrugated films might give us surprises.

Following our discovery of phonon-assisted photoemission process in graphene systems, it is important to verify this process in other systems. The hallmark of this process, i.e., phonon-induced gaps in the forbidden region, is normally very weak and can only be identified in a material that has a simple Fermi surface and a reasonable band gap. This is probably why such process has remained elusive in the photoemission community for a long time. Although these constraints for the material are strong, there are still many possible candidates for observing the phonon-induced gaps. One good candidate will be the Si(111) \( \sqrt{3} \times \sqrt{3} \) -Ag surface, whose Fermi surface simply consists of small pockets (surface state) at the \( \Gamma \) point of the superlattice. There are no other occupied states near the Fermi level, due to the Si band gap. Other systems with a circle-like Fermi surface should also exhibit phonon-induced gaps at the \( \Gamma \) point, if there is a real band gap near the Fermi level at the \( \Gamma \) point.

One possible application of the phonon-assisted photoemission is mapping the phonon dispersion relations. When the measurement is carried out along a high symmetry direction, where the gaps can be attributed to phonons with a single wave vector, the phonon dispersion relations could be directly mapped out.

The similarity between our ARPES spectra at normal emission and the tunneling spectra by STM is very intriguing. ARPES and STM are two complementary techniques (reciprocal space vs real space) and involve quite different physical processes (photoexcitation vs tunneling). Our study might help bridge the gap between these two measurements, at least for the case of graphene systems. Hypothetically, this connection have two prerequisites: (1) The material is 2D and has a reasonable band gap near the Fermi level at the zone center; (2) The STM tunneling current is well collimated perpendicular to the sample surface and the tip has a simple density of states. When both conditions are fulfilled, the similarity between the normal emission in ARPES and the tunneling spectrum in STM might be expected due to the same phonon-assisted process.
Currently, this connection is only a bold guess and further experimental evidences are needed in other systems. Interestingly, high-$T_c$ cuprates are in this category and tunneling spectra of these materials do show a gap in the normal state, known as the pseudogap. There have been lots of debates about its origin and its potential role in high-$T_c$ superconductivity. Is the pseudogap similar to the gaps observed in graphene? Well, the answer to this question requires further experimental investigation.
Appendix

Appendix A.1 Surface Brillouin Zone of FCC (111) Plane

This dissertation primarily deals with the FCC (111) surface. The FCC lattice can be viewed as a closed-packed structure with an ABC stacking sequence (Fig. A.1). The top view of this surface is shown in Fig. A.1(b). Note that the FCC (111) surface has a three-fold symmetry, i.e., [\(\text{[1\overline{1}2}\)] direction is not the same as [\(\text{[11\overline{2}]\)] direction. It is obvious from Fig. A.1(b) that a slight miscut of the (111) surface towards the [\(\text{[1\overline{1}2]\)] direction leads to straight step edge running along the [\(\text{[1\overline{1}0]\)] direction.

When surface sensitive measurements are carried out on the surface, e.g., RHEED, it is more convenient to use the 2D Bravais lattice (the top layer), instead of the 3D bulk Bravais lattice. The surface Brillouin zone can be simply understood as the Brillouin zone of the 2D Bravais lattice. A more rigorous way of defining the surface Brillouin zone is shown in Fig. A.2. The surface Brillouin zone is hexagonal. The corners are called \(\overline{K}\) points, and the middle points of the sides are called \(\overline{M}\) (\(\overline{M}'\)) points.

Appendix A.2 Fermi Surface Mapping

Fermi surface mapping is performed by recording the photoemission data at various sample angles. Fig. A.3 shows the experimental geometry in our system. We have four parameters for each electron detected by the analyzer, namely \(KE\) (kinetic energy in vacuum, in unit of eV), \(\theta_a\) (emission angle detected by analyzer, in the y-z plane), \(\theta\) (sample flip angle), \(\phi\) (manipulator rotation angle, which is essentially the sample rotation angle along y axis). A straightforward derivation yields the following relation:

\[
\begin{pmatrix}
  k_x \\
  k_y
\end{pmatrix} = 0.512\sqrt{KE} \begin{pmatrix}
  \sin \phi \cos \theta \\
  \cos \theta \sin \theta - \sin \theta \cos \phi \cos \theta
\end{pmatrix}.
\]

(A.1)

where \(k_x\) and \(k_y\) are the in-plane wave vectors of the detected electron in unit of \(\text{Å}^{-1}\), and \(KE\) is in unit of eV.
FIGURES

Figure A.1. (a) FCC lattice. (b) Top view of the truncated (111) plane of a FCC lattice. The inset shows the direction within the (111) plane.

Figure A.2. (a) Brillouin zone for FCC lattice. (b) Surface Brillouin zone corresponding to the FCC (111) surface.
Figure A.3. Experimental geometry for Fermi surface mapping in our system. The analyzer slits are fixed in the y-z plane. The electrons emit along the OA direction (in the y-z plane). The sample normal is along the OC (OZ’) direction, and the OY’ direction is parallel to the sample surface. The sample can be rotated along the y axis (\(\phi\)). At a fixed rotation angle \(\phi\), flipping the sample by \(\theta\) changes the sample normal from the OB direction (in the x-z plane) to the OC direction.
Author’s Biography

Yang Liu was born on August 8, 1981 in Yiyang, a city in the southern part of China. In 2000, he enrolled at University of Science and Technology of China (USTC) through the National College Entrance Examination. He graduated magna cum laude in 2004 with a B.S. in Physics. He enrolled at the University of Illinois at Urbana-Champaign in 2004, earning his Ph.D. in Physics in 2010. He received the Aladdin Lamp Award for dissertation research at the Synchrotron Radiation Center in Stoughton, Wisconsin.

Publications


