



Electronic and atomic structure of wide band gap GaN and thin aluminum adlayer studied with synchrotron radiation
by Cui Chen

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:

Photoemission using synchrotron radiation has been used to study the electronic and atomic structures of the wide band gap semiconductor GaN surface and metal-GaN interfaces.

Angle resolved interband-transition measurements were made for normal emission as a function of photon energy and off-normal emission as a function of both photon energy and polar angle. Valence band dispersion along three major symmetry lines $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Lambda K$ of the Brillouin-zone were obtained and compared to the theory. Good agreement was found between the experimentally mapped valence bands and the calculated bands. An occupied surface state is found just below the valence band maximum which is independent of the perpendicular wave vector and also shows sensitivity to adsorbed species.

Atomic termination of the GaN surface is determined by ion scattering spectroscopy. The spectra clearly show a Ga-terminated surface. The local site symmetry for aluminum is determined from photon-energy-dependent photoelectron-diffraction data which are inverted by the holographic principle to obtain a real space image. This technique is a direct experimental measurement which is model independent. The transformed Al 2p emission data yield a real space image of the Al emitter's nearest neighbor atoms. The intensity of the transform shows that the Al has two inequivalent adsorption sites. One is directly above the surface Ga, the on-top site, and the other involves replacing the surface Ga, the replacement site. The replacement site is found to be more favorable upon annealing.

High resolution core-level photoemission with synchrotron radiation and LEED studies have been used to determine the growth morphology and electronic structures of the Al, Sb/GaN(0001) interface, and the interface upon annealing. The chemical reaction taking place at the Al sites on n^{+-} and p-type GaN(0001) is followed using the photoemission spectra of the Ga 3d and Al 2p core-levels as a function of overlayer coverage, both at room temperature and upon annealing. The formation of a Schottky barrier is followed by accounting for the line-shape changes, the shifts of the bulk Ga 3d core-level binding energy, the change of surface work function, and the deduced dipole voltage contribution to the Schottky barrier height.

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A thesis submitted in partial fulfillment
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MONTANA STATE UNIVERSITY
Bozeman, Montana

January 1998

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C4191

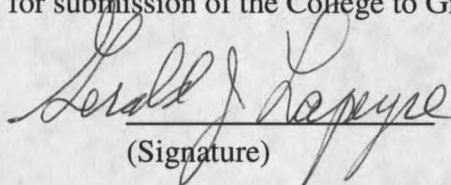
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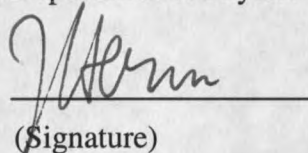
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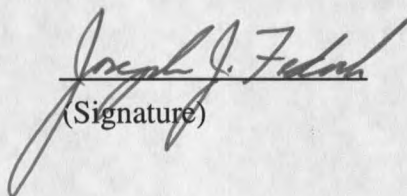
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ACKNOWLEDGMENTS

I am grateful for the guidance and support of my thesis advisor, Dr. Gerald J. Lapeyre. The way he approaches a physics problem, his ceaseless interest in the subject, and his broad knowledge were of great help in this thesis work. I wish to thank Dr. Mary E. Keeffe, daughter of Dr. Lapeyre, for her help in the initial work at the Wisconsin-Madison Synchrotron Radiation Center (SRC). I wish to thank Dr. Stephen Hill for his careful reading and correcting of this thesis. I wish to thank Dr. John C. Hermanson for his theoretical consultation and encouragement during the thesis work. I wish to thank Dr. Lisa Peterson for her help in the ion scattering spectroscopy measurement. I also acknowledge Dr. Richard J. Smith, Dr. Recep Avci, and Dr. James R. Anderson for their experimental consultation and their encouragement.

Thanks also to J. M. Van Hove at SVT Associates (Eden Prairie, MN) for growing and providing the GaN samples used in this thesis work. Thanks to Dr. Cliff Olson at SRC for his valuable advice on the beam-line and for experimental consultation and help. Thanks to all the SRC staff for their cheerful help over the hard working days of data collection. Thanks to the help of electronic technician Erik Andersen and machinist Norman Williams for helping to construct the experimental apparatus.

Finally, thanks to my husband Hao Ding for his encouragement, support and patience over the years of this endeavor.

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ABSTRACT

Photoemission using synchrotron radiation has been used to study the electronic and atomic structures of the wide band gap semiconductor GaN surface and metal-GaN interfaces.

Angle resolved interband-transition measurements were made for normal emission as a function of photon energy and off-normal emission as a function of both photon energy and polar angle. Valence band dispersion along three major symmetry lines $\Gamma\Delta\Delta$, $\Gamma\Sigma M$ and ΓAK of the Brillouin-zone were obtained and compared to the theory. Good agreement was found between the experimentally mapped valence bands and the calculated bands. An occupied surface state is found just below the valence band maximum which is independent of the perpendicular wave vector and also shows sensitivity to adsorbed species.

Atomic termination of the GaN surface is determined by ion scattering spectroscopy. The spectra clearly show a Ga-terminated surface. The local site symmetry for aluminum is determined from photon-energy-dependent photoelectron-diffraction data which are inverted by the holographic principle to obtain a real space image. This technique is a direct experimental measurement which is model independent. The transformed Al 2p emission data yield a real space image of the Al emitter's nearest neighbor atoms. The intensity of the transform shows that the Al has two inequivalent adsorption sites. One is directly above the surface Ga, the on-top site, and the other involves replacing the surface Ga, the replacement site. The replacement site is found to be more favorable upon annealing.

High resolution core-level photoemission with synchrotron radiation and LEED studies have been used to determine the growth morphology and electronic structures of the Al, Sb/GaN(0001) interface, and the interface upon annealing. The chemical reaction taking place at the Al sites on n^+ - and p -type GaN(0001) is followed using the photoemission spectra of the Ga 3d and Al 2p core-levels as a function of overlayer coverage, both at room temperature and upon annealing. The formation of a Schottky barrier is followed by accounting for the line-shape changes, the shifts of the bulk Ga 3d core-level binding energy, the change of surface work function, and the deduced dipole voltage contribution to the Schottky barrier height.

CHAPTER 1

INTRODUCTION

Great effort and significant progress have been made in the crystal growth of wide band gap semiconductors with band gaps greater than 2.3 eV in recent years ¹⁻⁷. The fabrication of high-temperature (>600°C) high-power and high-frequency optoelectronic devices, such as high-brightness GaN/InGaN blue light emitting diodes ⁸ (LEDs), have been made possible based on the physical properties of these materials. The direct transition in GaN and its complete miscibility with AlN and InN gives greater efficiencies in optoelectronic devices than those of indirect-band-transition semiconductors ⁹. Blue GaN-based diode lasers were achieved by Nakamura et al. ¹⁰ in 1996. Nevertheless, very little experimental work has been done on the fundamental electronic properties of these materials. The primary goals of this thesis work are to investigate the electronic properties of the GaN(0001) surface and of metal/GaN interfaces by angle-resolved and angle-integrated photoemission spectroscopy and by photoelectron holographic imaging (PHI).

Review of GaN Work ^{9,11}

Johnson, Parsons, and Crew ¹² first synthesized GaN in 1932 and Juza and Hahn reported the structure to be wurtzite in 1938. ¹³ Unlike other Ga-V semiconductors (GaP, GaAs, GaSb) which have a cubic zinc-blende structure, GaN can appear in either wurtzite,

zinc-blende, or a mixture of the two structures, with the wurtzite structure being more stable. Wright¹⁴ used a plane-wave pseudopotential (PWPP) method to calculate the total energy and found that the energy is higher for zinc-blende than for wurtzite by 22 meV per GaN unit. Fig. 1.1 (see also Fig. 2.9) shows the wurtzite and zinc-blende configurations along the c-axis ($[0001]$ or $[000\bar{1}]$) and $[111]$ directions, respectively. The three atoms bonded at one end of the bond are aligned with the three atoms at the other end of the bond in the wurtzite structure and not aligned (rotated 60°) in the zinc blende structure. The correspondence between the valence bands of the two structures can be found in references.^{15,16,17,18,19}

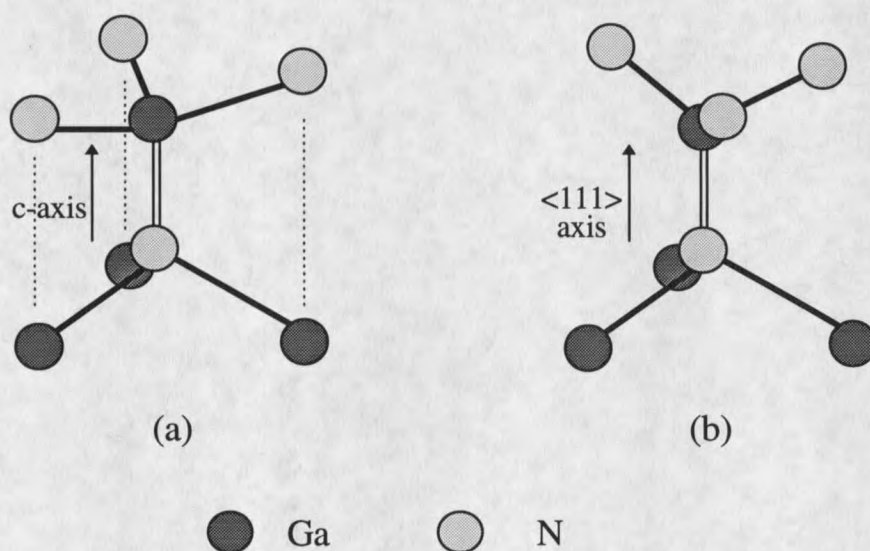


Fig. 1.1 Atomic arrangements in (a) wurtzite and (b) zinc blende structures.

Single-crystal GaN wafers are not commercially available. The most common growth methods are Molecular Beam Epitaxy¹⁻⁴ (MBE), with a nitrogen plasma source,

Organometallic Vapor Phase Epitaxy ⁵ (OMVPE), or Metalorganic Chemical Vapor Deposition ⁶⁻⁷ (MOCVD) on a sapphire or silicon carbide substrate. Ammonia is the most commonly used plasma source for the above growth methods and the deposition temperature is usually greater than 950°C. High temperatures are needed to break up the tight N-C bonds. The film thickness grown is typically ~1 μm .

The high doping level (typically $\geq 10^{18}\text{cm}^{-3}$) of n-type GaN is believed to be caused by nitrogen vacancies ⁹ which are found to lie roughly 40 meV below the conduction band. At high epitaxy temperatures (900-1050°C), the following reaction can lead to the nitrogen vacancies :



There have been many GaN band calculations in the literature. Treating the Ga 3d shell as an inert core of electrons using pseudopotential calculations, versus including the Ga 3d valence electrons (all-electron calculations) are the two main theoretical approaches in the calculation of the bands. Because of the proximity of Ga 3d to the N 2s or 2p states, hybridization between these states will change the valence band (VB) structure, especially the lower part of the VB with initial energy about -15 eV relative to valence band maximum (VBM).²⁰ To experimentally determine the GaN valence band structures with synchrotron radiation is one of the primary goals of this work.

The metal-GaN interface has important applications in device fabrication. The latter parts of this thesis will focus on the Al/GaN interface, both at low (~0.5 monolayer) and high (~8 monolayer) Al coverage.

Angle-Resolved Photoemission²¹

Photoemission spectroscopy is a technique to experimentally measure the kinetic energy of electrons emitted by absorption of photons, as depicted in Fig. 1.2. The energy of a photoemission process for a semiconductor is usually referenced to the VBM. Photons with high enough energy excite electrons which may eventually escape from the sample to be registered at the detector. If the detector collects most of the signal from the emission hemisphere above the sample, then the photoemission spectra are called angle-integrated. In order to measure both the energy and direction of the photoemitted photoelectron, one can reduce the angular acceptance of the detector. This angle-resolved photoemission (ARP) has been employed extensively to study all kinds of metals and semiconductor surfaces since the late 70's until the present day. Consequently, microscopic electronic properties, such as band structures, become obtainable in the laboratory rather than just existing in theory. The utilization of an intense synchrotron radiation source, with its continuum of polarized photons, further opened up the scope of ARP experiments beyond what would have been possible with conventional ultra-violet (UV) lamps and x-ray sources.

Photoelectron Diffraction Imaging (PDI)

While electronic structures of solids can be determined by angle-resolved photoemission in reciprocal space, another approach involving photoelectron diffraction can be used to obtain the atomic geometric structure directly.

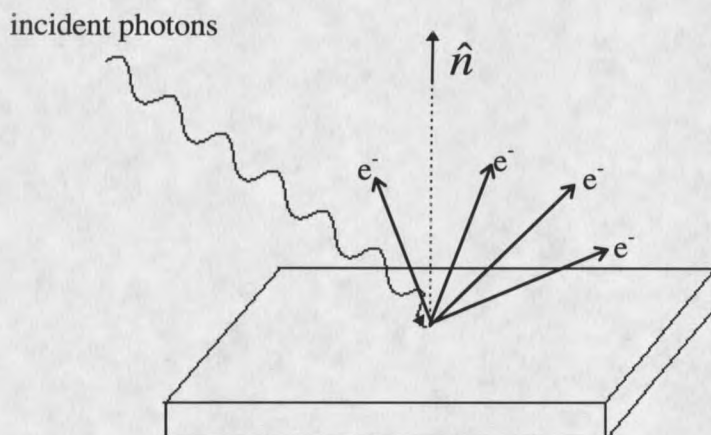


Fig. 1.2 Photoemission process.

At relatively high energies (greater than several hundreds of eV), the scattering process of photoelectrons produces enhanced intensities along directions connecting the emitting atoms with overlying nearest and next-nearest neighbor atoms, the so called forward scattering effect,²² as depicted in Fig. 1.3. This is, thus, an effective tool for studying surface alloying, inter-diffusion, orientation of adsorbed molecules, and so on.

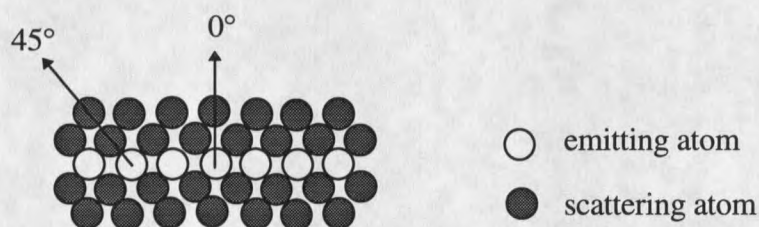


Fig. 1.3 Schematic drawing of forward scattering.

A recent powerful technique, obtained by transforming photoelectron diffraction data, can be utilized to determine the local three-dimensional structure directly without dependence on any model. First proposed by Szöke in 1986, electron holography can be achieved with photoelectrons or Auger decay electrons. Barton simulated a photoelectron hologram in 1988 for S 1s photoemission from a $c(2 \times 2)$ S/Ni(001) surface. In standard terminology, the reference wave results from direct photoemission from the emitter S 1s, and the object wave scatters from nearby Ni atoms (scatterer). This produces a diffraction pattern, as depicted in Fig. 1.4. By Fourier-like transformation, a three-dimensional image of the surface structure surrounding the emitter S on the ordered surface can be obtained.

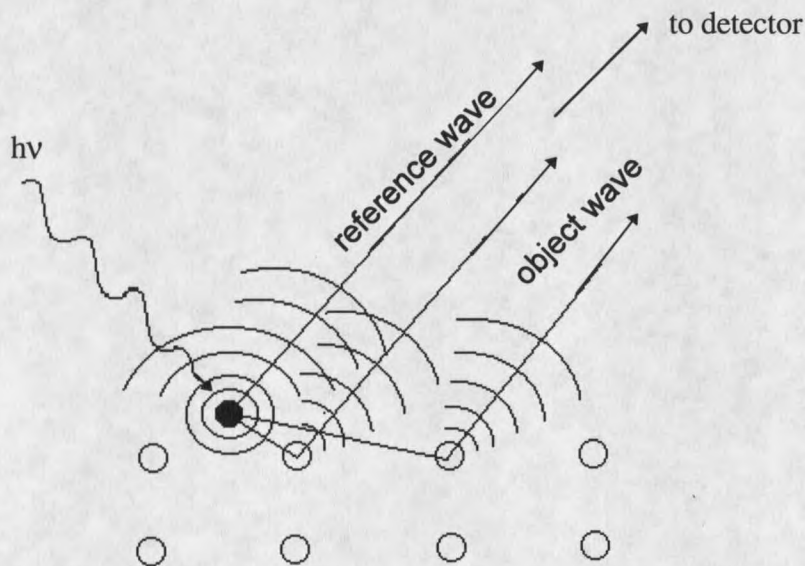


Fig. 1.4 Schematic representation of a photoelectron hologram by two processes contributing to the photoemission measured from an ionized adsorbate atomic core-level (dark atom).

Images using single-energy holography (SEH) were obtained experimentally by Harp et al. in 1990. The diffraction patterns were transformed over the emission directions only and showed twin images (image at both the real atom position and the position inverted about the emitter) and significant artifacts.

In 1992 S. Y. Tong et al. proposed energy-dependent photoelectron-diffraction.²³ By measuring a series of diffraction patterns as a function of photon energy, each with different emission angles θ and ϕ on the emission hemisphere, a three-dimensional structure can be obtained from atoms within the mean-free path of the outgoing photoelectrons. This method has solved the twin-image problem, improved the image position accuracy and, most importantly, significantly reduced artifacts. Wu et al.²⁴ were the first to experimentally implement this method and demonstrated the striking power of the technique in obtaining the three-dimensional atomic structures directly on a $\sqrt{3} \times \sqrt{3}$ Al/Si(111) system. To further reduce the artifacts of this technique, Wu et al. proposed the small-cone method,²⁵ which significantly improved the image quality even further (reduced artifacts, cleaner image), by using of only the part of the transformed diffraction data that contributed most to the final image.

Metal-Semiconductor Interface

The Schottky barrier height (SBH) plays a crucial role in determining the performance of many electronic devices. A detailed understanding of Schottky barrier formation is a very complex issue and much theoretical and experimental work has been done to elucidate the

Schottky barrier formation mechanism. Before the experimental results and discussions are presented, some historical review would be helpful.²⁶ In 1939 Schottky²⁷ first proposed the work-function-difference model, which is based on the assumption that the potential difference between the Fermi levels of metal and semiconductor falls entirely across the space charge region within the semiconductor surface. By 1947 there was strong experimental evidence indicating that the predicted dependence of the Schottky barrier height on the metal work function did not occur. Therefore, Bardeen²⁸ proposed that, in covalent semiconductors, intrinsic surface states of sufficiently high density in the band gap stabilize or "pin" the Fermi level and, thus, the Schottky barrier height is largely independent of the metal. In the mid sixties Heine²⁹ suggested that metallic-like states with wave functions decaying into the semiconductor are responsible for the Fermi-level pinning. In the mid seventies, Chye et al.³⁰ demonstrated that there can even be Fermi-level pinning without the presence of intrinsic surface states in the band gap. Later on, it was shown that less than $10^{12}/\text{cm}^2$ metal-induced states are sufficient to pin the Fermi level.^{5,26}

Rowe et al.³¹ did much work on group III metals on GaAs, Ge and Si and suggested that the metal forms covalent bonds to the semiconductor surface which give rise to the observed metal-induced states. For more-ionic semiconductors, Mead and Kurtin et al.³² observed a strong dependence on the overlayer metal used and showed that the separation between covalent and ionic behavior came at an electronegativity difference of 0.6. The index of interface behavior, S , is then defined as $S = d\phi_b / d\chi_M$, where χ_M is the metal electronegativity and ϕ_b the electron barrier height. For covalent semiconductors $S \sim 0.1$, and for insulators $S \approx 1$ or ≥ 1 . For more ionic compounds with higher heat of formation, fewer

defects are formed, therefore the dependence on the metal work function is much stronger.²⁶ On the other hand, for covalent semiconductors Mead and Spitzer³³ showed a "two-thirds" rule often applies, i.e. the barrier height is approximately two thirds of the energy gap E_g .

McCaldin et al.³⁴ has shown that for III-V and II-VI compounds the Schottky barrier height for holes is dependent only on the particular anion and is approximately a linear function of anion electronegativity. This "anion rule" also applies to materials that do not follow the two-thirds rule, and to more ionic compounds such as ZnS which has $S \approx 1.0$.

Brillson et al.³⁵ proposed a model in the late seventies in which both the band bending and the interfacial dipole, resulting from the ionicity of the chemical bonding between the metal and semiconductor atoms, contribute to the barrier height. Hughes et. al.³⁶ showed that the surface Fermi level is pinned at the same level within the gap for both n- and p- type Mn on GaAs(110) and V on GaAs(110) after only one tenth of an Ångstrom of metal coverage. This suggested a transition metal impurity state being responsible for the pinning of Fermi level at the interface and ruled out the unified defects model^{37,3} which would give rise to two separate Fermi-level pinning positions for n and p-type material.

In the late eighties and nineties, the desire to have a better understanding of Schottky barrier formation of various metal-semiconductor interfaces has continued. For example, W. E. Spicer et al.³⁸ have proposed the advanced unified defect model (1988) and J. Ortega et al.³⁹ have performed a theoretical analysis of Schottky barrier height as a function of Al coverage on GaAs(110).

CHAPTER 2

THEORY

Photoemission Spectroscopy and Band TheoryOne-Electron Model and Band Theory⁴⁰

The total Hamiltonian for a solid consists of the kinetic energy of the electrons and ionic cores, the core-core, electron-electron, and electron-core Coulomb interactions as well as relativistic effects. By assuming fixed cores in the band structure calculations and by using the Born-Oppenheimer approximation,^{41,42} which allows a decoupling of the core and electron parts,^a the Hamiltonian can be written as:

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{n,i} V_n(\vec{r}_i - \vec{R}_n) \quad (2-1)$$

^a Assuming the electronic wave function varies slowly with internuclear distance, then the total wave function can be written as the product of the electronic part ϕ_e and vibrational part ϕ_v of the molecule. The probability of excitation from a molecular ground state v to ionic vibrational state v' is given by the Born-Oppenheimer approximation as:

$$I(\text{photocurrent}) = |M_e|^2 \left| \int \Phi_v \Phi_{v'}^* d\tau \right|^2$$

where M_e is the transition matrix element, determined by the electronic wave functions and transition operator.

The first term is the kinetic energy of the electrons with momentum $\mathbf{p}$, the second term is the electron-electron Coulomb interaction and the last term is the Coulomb interaction between an electron (at $\mathbf{r}_i$) and the core (at $\mathbf{R}_n$). This many-body problem is very hard to solve. A major simplification involves using Hartree mean-field theory to reduce the problem to a one-electron model. By assuming that each electron moves in the average field produced by all the other electrons, the Hamiltonian becomes:

$$H = \sum_i H_i = \sum_i \left\{ \frac{p_i^2}{2m} + V(\vec{r}) \right\} \quad (2-2)$$

where $V(\mathbf{r})$ has the symmetry of the lattice and consists of both electron-electron and electron-core interactions.

The one-electron Schrödinger equation and boundary conditions imposed by the periodicity of the lattice are:

$$\begin{aligned} \left[\frac{p^2}{2m} + V(\vec{r}) \right] \psi(\vec{r}) &= E \psi(\vec{r}) \\ V(\vec{r}) &= V(\vec{r} + \vec{R}_n) \end{aligned} \quad (2-3)$$

The solutions are:

$$\begin{aligned} \psi_{\vec{k}}(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) \\ u_{\vec{k}}(\vec{r}) &= u_{\vec{k}}(\vec{r} + \vec{R}_n) \end{aligned} \quad (2-4)$$

Theoretical calculations of $E(\mathbf{k})$ are often made by means of pseudopotentials. The major virtue of this approach is that only the valence electrons need to be considered. The

ionic cores are assumed frozen in an atomic-like configuration. The valence electrons move in a net, weak one-electron potential:

$$\left[\frac{p^2}{2m} + V_c + V_R\right]\phi = \left[\frac{p^2}{2m} + V_{pseudo}\right]\phi = E\phi \quad (2-5)$$

where V_{pseudo} is the pseudopotential, which is the sum of the attractive long-range core potential V_c and the short-range repulsive potential V_R .

One example of the pseudopotential method is the orthogonalized plane wave (OPW) method. The expansion coefficients used to ensure that the plane wave part of an OPW function is orthogonal to the core states can be grouped to construct an orthogonality potential. This potential is repulsive because its effect is to keep the valence electrons out of the core. If the repulsive potential is added to the attractive core potential, they will almost cancel out, leaving a net weak pseudopotential. This pseudopotential can then be used to solve the Schrödinger equation.

To include both the long-range attractive core potential and short-range repulsive potential, different simple model potentials or empirical potentials can be used to compute the electronic band structure. One such simple model potential is:

$$V(r) = \begin{cases} -\frac{Ze}{r}, & r > r_c \\ -\frac{Ze}{r_c}, & r \leq r_c \end{cases} \quad (2-6)$$

where Z is the valence of the atomic species, for example, $Z = 4$ for silicon.

The two most common methods for computing $E(\mathbf{k})$ are the tight-binding method (TBM), which is also called the linear combination of atomic orbital method (LCAO), and the nearly free-electron model (NFEM). The TBM method emphasizes the atomic-like nature of the electronic states while the NFEM method views the valence electrons as a perturbed gas of nearly free electrons. The major feature of the NFEM are: the weak potential; a plane-wave basis set; and free-electron bands except near the BZ boundaries and band crossings.

In the free-electron model, the free-electron energies are given by (extended zone scheme):

$$E(\vec{k}) = \frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 \quad (2-7)$$

Fig. 2.1 shows the free-electron band structure (also called an "empty lattice") drawn in solid lines and the NFEM band structure modifications drawn in dashed lines. The NFEM gives rise to a band gap of $2|V(\vec{G})|$ at the Brillouin-zone boundary k_{bz} and band crossings.

$V(\mathbf{G})$ is the Fourier component of the crystal potential. The four number indices in Fig. 2.1 are the $\mathbf{G}$ vector values.

While many calculated electronic structures of wurtzite GaN are available in the literature, ⁴³ experimental studies of the band structure of GaN are very scarce. Angle-resolved photoemission (ARP), using a synchrotron radiation source, provides the possibility to obtain the three dimensional band structure of solids. With photoemission, incident photons give electrons in a solid the energy required to reach excited states, and the crystal potential imparts the momentum needed to reach these excited states in units

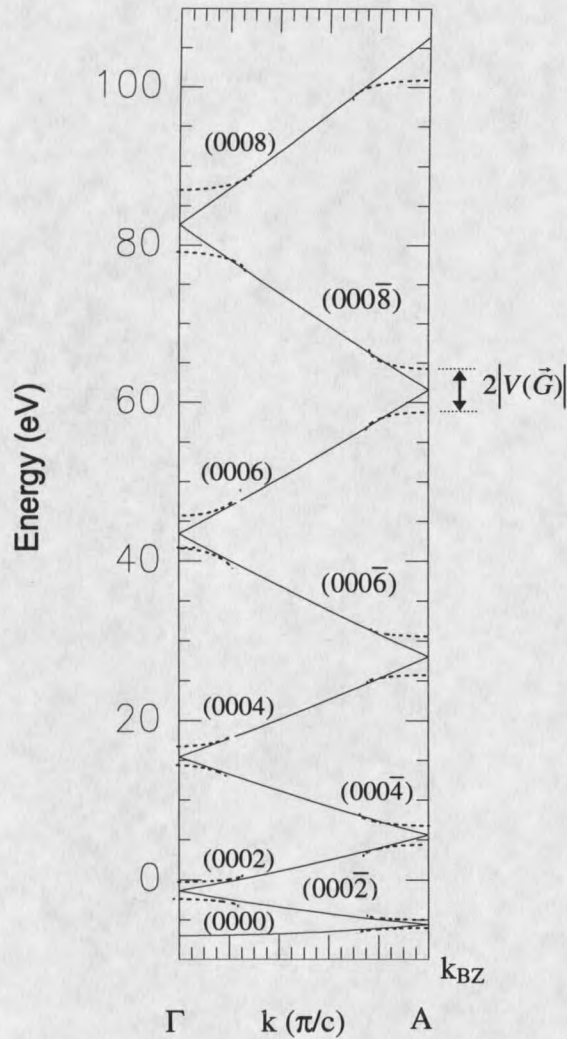


Fig. 2.1 The free-electron band structure drawn in solid lines and the NFEM band structure modifications drawn in dashed lines. The NFEM band structure has a band gap at the BZ boundary k_{BZ} and band crossings.

of the reciprocal lattice vector $\mathbf{G}$. A continuum synchrotron radiation source allows one to be able to probe a large range of k -space, and by the symmetry of the lattice, this gives a rigid test of the repeated dispersions along high symmetry lines of the Brillouin-zone.

In angle-integrated mode, the solid angle of detection is large (close to 2π under favorable conditions), which smears the $\mathbf{k}$ -directional information by the integration of all the outgoing wave vectors. The direct transitions (with $\mathbf{k}_i = \mathbf{k}_f = \mathbf{k}$ in the first Brillouin-zone) between two bands (initial and final bands $E_i(\vec{k})$ and $E_f(\vec{k})$) are positioned on a single surface in $\mathbf{k}$ -space:

$$\Omega_{fi}(\vec{k}) = E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega = 0 \quad (2-8)$$

The joint density of states is obtained when $\mathbf{k}$ -integration is performed for a surface of constant interband energy:

$$J(\hbar\omega) = \frac{1}{(2\pi)^3} \sum_{i,f} \int \delta(\Omega_{fi}(\vec{k})) d^3\vec{k} \quad (2-9)$$

The quantity $J(\hbar\omega)$ gives the total number of direct transitions that are possible for a particular incident photon energy. Now the energy distribution of the joint density of states is integrated over the whole Brillouin-zone (BZ):

$$D(E, \hbar\omega) = \frac{1}{(2\pi)^3} \sum_{i,f} \int \delta(\Omega_{fi}(\vec{k})) \delta(E_{KE} - E_f + \phi) d^3\vec{k} \quad (2-10)$$

where $\delta(E_{KE} - E_f + \phi)$ selects the transitions that involve the final energy E_f , and ϕ is the energy difference (work function) from the Fermi level to the vacuum level.

With ARP, one measures $\vec{k}^{out}$ which, in some cases (see discussions later) could be “mapped” to get $\vec{k}^{in}$, a point in the reduced BZ. Fig. 2.2 shows schematics of the photoelectron momentum inside and outside the crystal. Across the crystal surface, the

parallel component of electron wave-vector is conserved up to a reciprocal lattice vector

$\mathbf{G}$:

$$\mathbf{k}_{\parallel}^{\text{out}} + \mathbf{q} = \mathbf{k}_{\parallel}^{\text{in}} + \mathbf{G}_{\parallel} \quad (2-11)$$

where $\mathbf{q}$ is the photon wave-vector, which is much smaller than the electron wave-vector

$\mathbf{k}$, and in the reduced Brillouin-zone scheme, $\mathbf{G} = 0$.^b Approximately, then,

$$\mathbf{k}_{\parallel}^{\text{out}} = \mathbf{k}_{\parallel}^{\text{in}} \quad (2-12)$$

For metals, one usually chooses the Fermi level as the electron-energy reference level. For semiconductors, however, the Fermi level is no longer a good reference level, since it strongly depends on the doping type, doping level, surface and interface states,

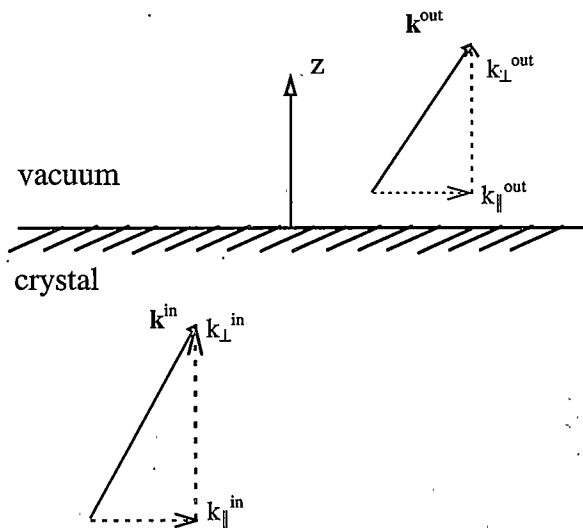


Fig. 2.2 Photoelectron momentum inside and outside the crystal.

^b $q = h/\lambda$, the λ 's associated with photons are a few orders of magnitude larger than that of λ 's associated with the lattice constants.

and various surface treatment processes. Thus for semiconductors, the valence band maximum (VBM) is usually chosen as the reference level. The following equations and discussions will assume the VBM as the reference level. Fig. 2.3 shows the various electron energy levels in a photoemission process.

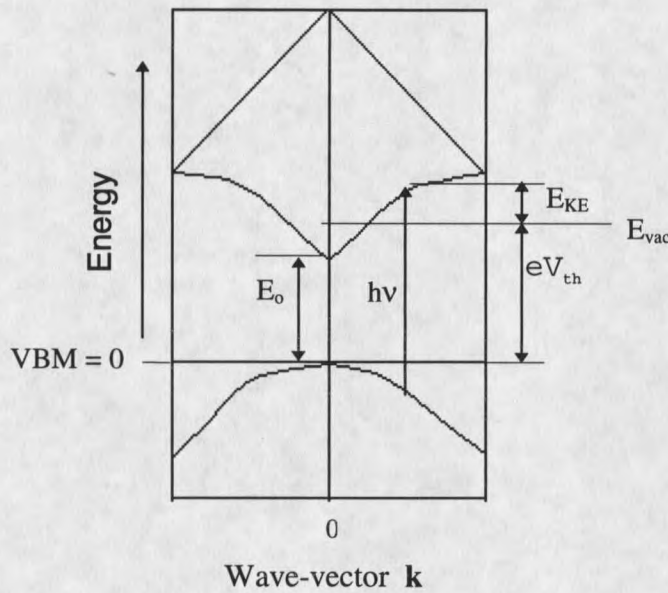


Fig. 2.3 Various electron energy levels in a photoemission process.

Assuming a simple free-electron final state, we can relate the final-state energy outside the crystal $E_f(\vec{k})$ to that inside the crystal by:

$$E_f(\vec{k}) = \hbar^2(k_{\parallel}^2 + k_{\perp}^2) / 2m^* - |E_0| \quad (2-13)$$

where m^* is the effective mass, and E_0 is related to the inner potential V_0

($|V_0| = |E_0| + |eV_{th}|$). The above equation can be simply interpreted as a free-electron parabola approximation of the final states with the bottom of the parabola attached to the bottom of the conduction band at energy E_0 . Usually the free-electron mass m_0 is used for the effective mass m^* . V_0 (usually a negative number between -10 to -15eV) can be determined in three ways: 1) it is adjusted in such a way that the agreement between experimental and theoretical band structure, for the occupied states, is optimal, or 2) use the value of the theoretical muffin-tin zero,^c or 3) from the symmetries (various turning points at BZ boundaries) of the experimental dispersion curves $E(k_{\perp})$.

The measured kinetic energy E_k is related to E_f by:

$$E_f = E_k + e\Phi_{th} \quad (2-14)$$

where $e\Phi_{th}$ is the threshold for emission from valence band (VB), $e\Phi_{th} = E_{vac} - E_{VBM}$

Combining equations (2-13) and (2-14), we have:

$$E_K = \hbar^2 (k_{\parallel}^2 + k_{\perp}^2) / 2m \quad (2-15)$$

where V_0 is the inner potential, $V_0 = E_0 - e\Phi_{th}$

Energy conservation requires:

$$E_f(\vec{k}) = E_i(\vec{k}) + h\nu \quad (2-16)$$

where $E_i(\vec{k})$ and $E_f(\vec{k})$ are the initial and final state energies, and $h\nu$ the photon energy.

^c The crystal potential can be approximated for band structure calculations by a muffin-tin potential. The potential is represented by that of an isolated ion within a sphere of radius r_0 , with the ions centered around each lattice point. r_0 is chosen so that the spheres do not overlap. The potential outside the sphere is zero. This zero, with respect to the vacuum level, is often called the muffin-tin zero.

The perpendicular momentum inside the crystal can be obtained only if we know how the final state disperses. One way is to assume the calculated final state dispersion. Another method is to assume a free-electron parabolic dispersion for the final state, as expressed by equation (2-13). Then the momentum inside the crystal can be solved as:

$$\hbar k_{\parallel} = (2mE_k)^{1/2} \sin \theta = [2m(E_i + h\nu - e\Phi_{th})]^{1/2} \sin \theta \quad (2-17a)$$

$$\hbar k_{\perp} = [2m(E_k \cos^2 \theta - V_0)]^{1/2} = \{2m[(E_i + h\nu - e\Phi_{th}) \cos^2 \theta - V_0]\}^{1/2} \quad (2-17b)$$

For normal emission ($\theta = 0^\circ$), we have:

$$k_{\parallel} = 0 \quad (2-18)$$

$$\hbar k_{\perp} = [2m(E_i + h\nu - E_0)]^{1/2}$$

or more conveniently written as:

$$k_{\perp} = 0.512 \sqrt{E_k (eV)} \text{ (\AA}^{-1}\text{)} \quad (2-19)$$

The dispersions of $k_{\parallel}$ and $k_{\perp}$ in the extended Brillouin-zone are plotted in Fig. 2.4 and 2-5, with $k_{\parallel}$ along the ΓM $[10\bar{1}0]$ and ΓK $[01\bar{1}0]$ directions and with $k_{\perp}$ along the ΓA $[0001]$ direction for wurtzite GaN, in analogy to the work of E. W. Plummer and W. Eberhardt.⁴⁴ These graphs can be used to visualize and direct the ARP experiment conveniently. For example, to probe the M point in k space at $k_{\parallel} = 1.1372 \text{ \AA}^{-1}$ and $k_{\perp} = 6 \text{ \AA}^{-1}$, we need to set the polar angle $\theta = 20^\circ$ and kinetic energy about 42 eV, as read from Fig. 2.4.

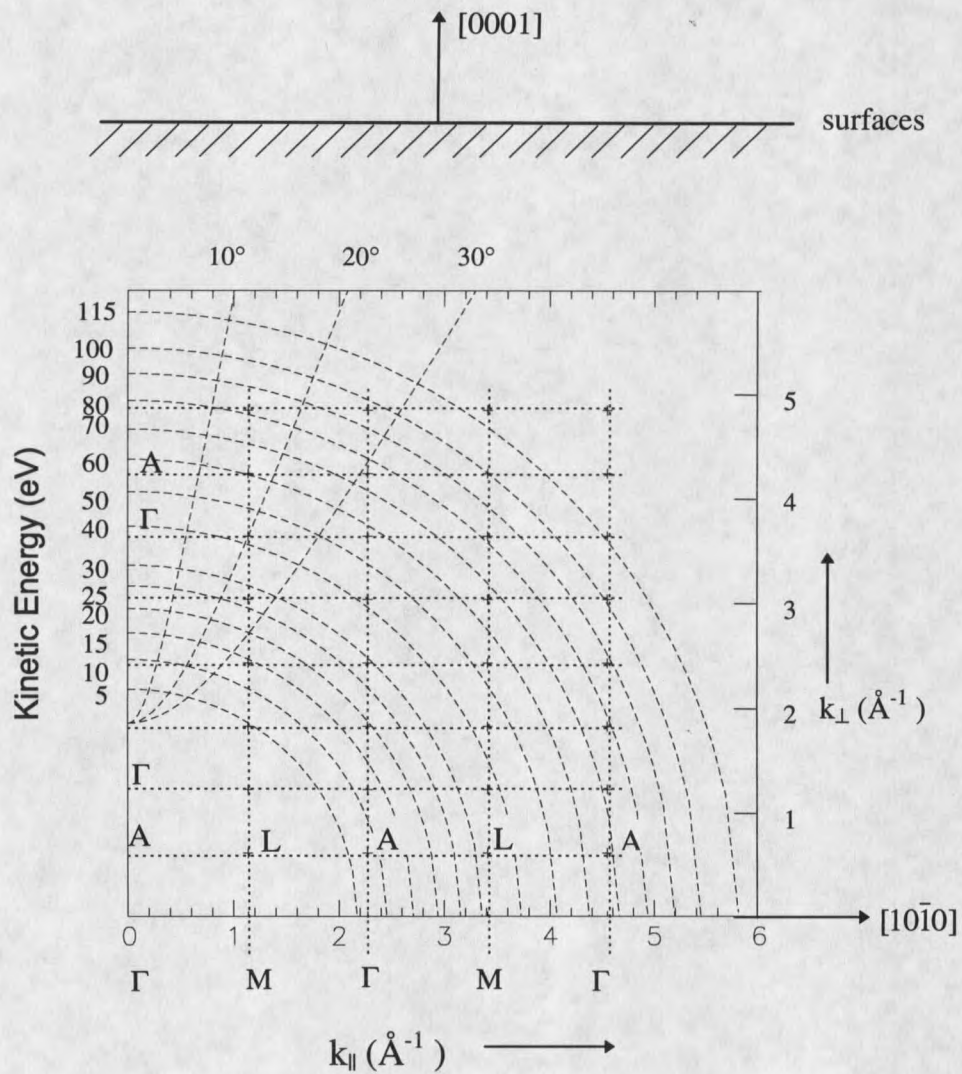


Fig. 2.4 The relationship for final-state values of $k_{\parallel}$ and $k_{\perp}$ in the free-electron extended Brillouin-zone, with $k_{\parallel}$ along ΓM $[10\bar{1}0]$ and $k_{\perp}$ along ΓA $[0001]$ directions of wurtzite GaN. The parabolic dashed lines represent equation (2-17) for $\theta = 10^\circ, 20^\circ, 30^\circ$.

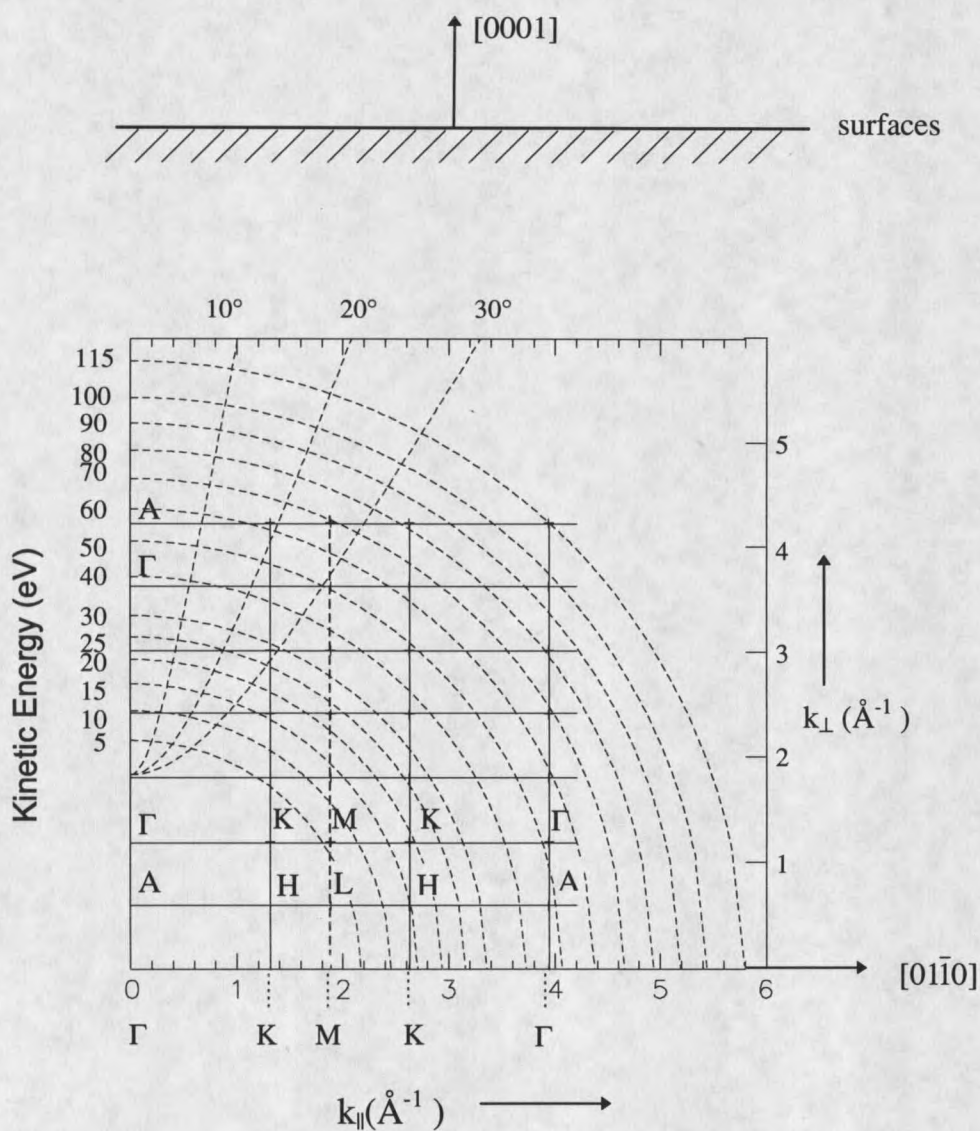


Fig. 2.5 The relationship for final-state values of $k_{\parallel}$ and $k_{\perp}$ in the free-electron extended Brillouin-zone, with $k_{\parallel}$ along ΓK $[01\bar{1}0]$ and $k_{\perp}$ along ΓA $[0001]$ directions of wurtzite GaN. The parabolic dashed lines represent equation (2-17) for $\theta = 10^\circ, 20^\circ, 30^\circ$.

Basic Modes of Photoemission Spectroscopy

There are three main modes of photoemission spectroscopy. These are energy distribution curve (EDC), constant initial state (CIS) and constant final state (CFS). Fig. 2.6 depicts the EDC mode and the associated electron energy levels. The kinetic energy of the emitted photoelectrons is the portion of the energy above the vacuum level:

$$E_{KE} = E_f - e\Phi_{th} \quad (2-20)$$

where $e\Phi_{th}$ is the threshold for emission from valence band maximum (VBM), $e\Phi_{th} = E_{vacuum} - E_{VBM}$

For a transition between initial state E_i and final state E_f , conservation of energy requires:

$$h\nu = E_f - E_i \quad (2-21)$$

combining equations (2-20) and (2-21), we have:

$$E_{KE} = h\nu - eV_{th} + E_i \quad (2-22)$$

where the initial state energy E_i is usually referenced to VBM (or Fermi level) and a negative number.

If the photon energy $h\nu$ is fixed, then when the kinetic energy is scanned from high to low energies, the collected signals will correspond to initial states of increasing binding energies (i.e. the absolute value of E_i increases), as is obvious from equation (2-22). The maximum kinetic energy in an EDC spectrum thus corresponds to the initial state with the lowest binding energy, which is the valence band maximum (VBM), as shown for photo-

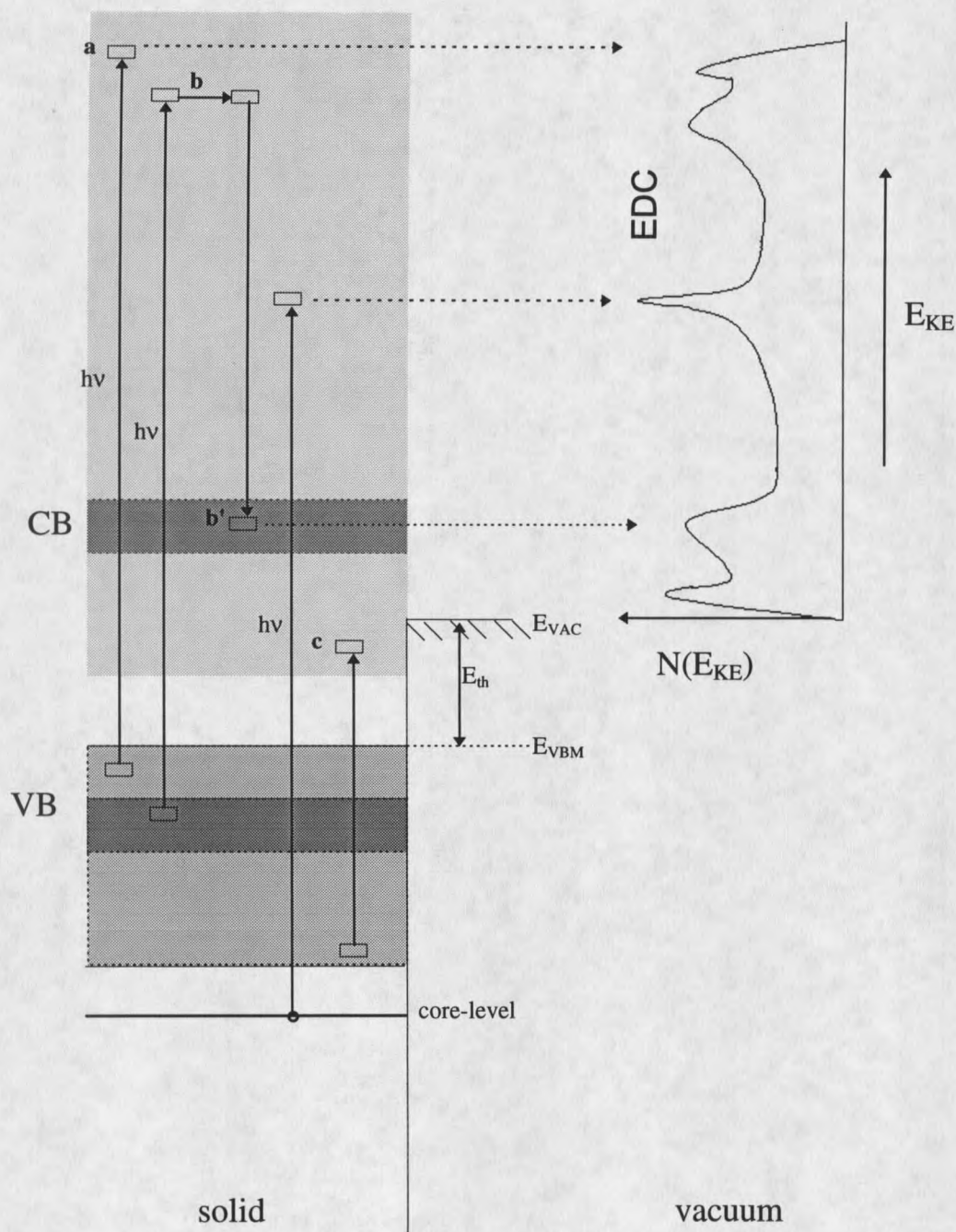


Fig. 2.6 Photoemission spectroscopy in energy distribution curve (EDC) mode. The maximum kinetic energy in a EDC spectra corresponds to initial state of lowest binding energy, which is the valence band maximum (VBM), as shown for photoelectron **a**. See text for more detail.

electron **a** in Fig. 2.6. For those electrons which undergo inelastic scattering, part of their energy will be lost; for example, electron **b** may impart some of its energy to electron **c**, thus giving rise to a secondary electron background of the EDC (**b'** in Fig. 2.6). Electron **c** which is excited to the conduction band (CB) by electron **b** may have energy below the vacuum level (E_{VAC}) and so would not be registered at the detector.

The measured kinetic energy zero in a EDC spectrum does not always exactly match the spectrometer's vacuum level E_{vac} . For example, in a low carrier density semiconductor sample, surface charging can occur due to excessive positive charges left behind, which is due to an insufficient electron replenishment from a low doping semiconductor sample. In this case, the outgoing photoelectrons will be more strongly bound and their resultant kinetic energy will be lower. This would shift the whole EDC curve to lower kinetic energy, leading to a cutoff of the lower end of the EDC corresponding to the vacuum level. This is sometimes called the "invisible wall" problem. In order to correct this problem, a negative bias (-2 to -5 volts) is usually applied to the sample.

If we change photon energy and the corresponding kinetic energy window simultaneously, then the initial state energy will be a constant, as is obvious if we rewrite equation (2-22) as:

$$E_i = E_{KE} + eV_{th} - h\nu \quad (2-23)$$

The constant initial-state-energy spectrum (CIS) mode is depicted in Fig. 2.7. Later we will discuss the photoelectron diffraction imaging (PDI) technique, where all the data are taken in CIS mode. A particular core-level initial state (2p or 3d) from an overlayer atom

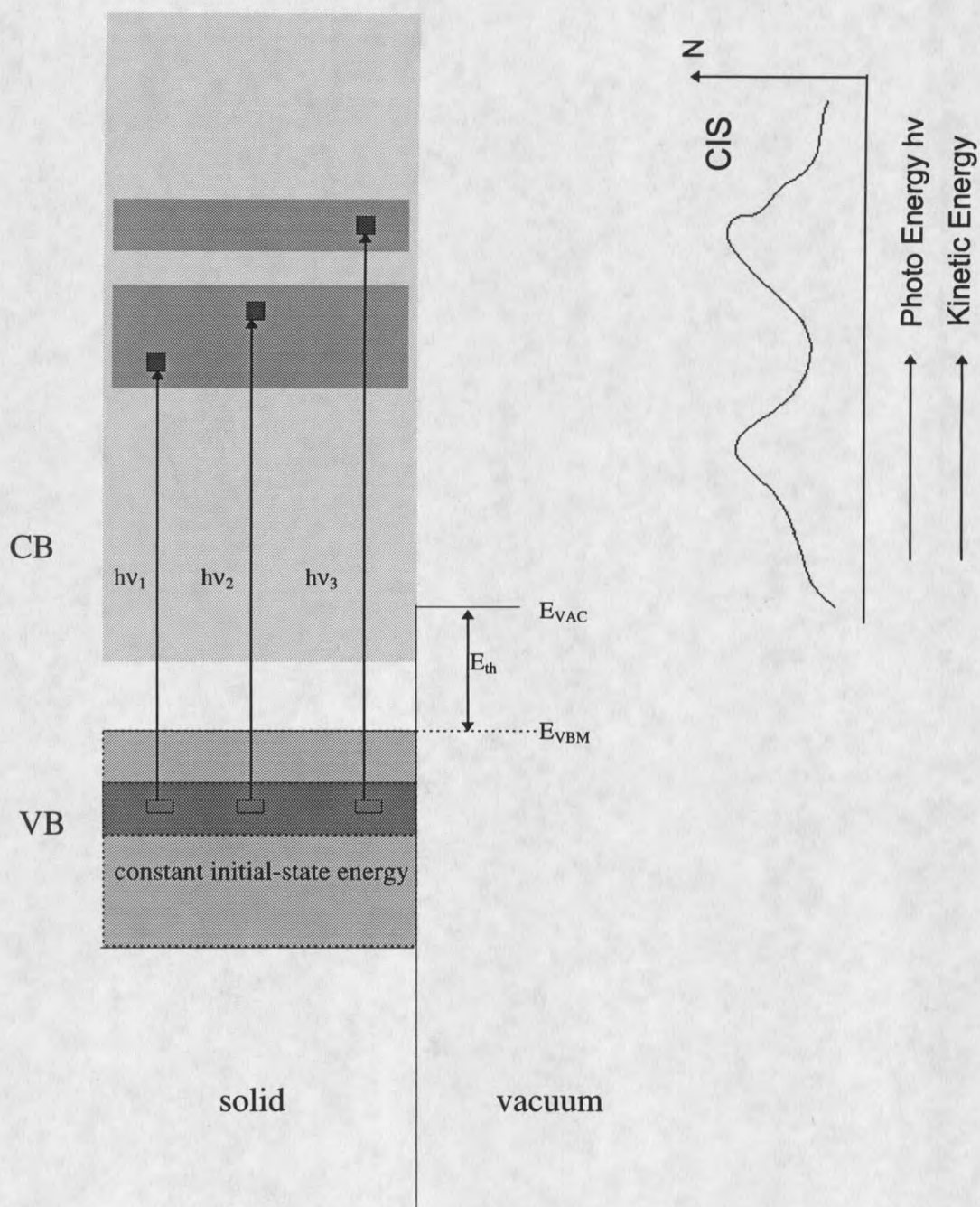


Fig. 2.7 Photoemission spectroscopy in constant initial-state-energy spectrum (CIS) mode.

is usually chosen for the CIS, which contains the diffraction information from the waves scattered by the atomic species nearby an overlayer atom.

Finally, the constant final-state-energy spectrum (CFS) is achieved by sweeping photon energies and keeping the kinetic energy fixed, as depicted in Fig. 2.8. Generally, photoemission spectroscopy is used to determine the density of occupied states, while optical ⁴⁵ and electron-energy-loss spectroscopy ⁴⁶ are used to determine transitions from core-levels to unoccupied states. With photoemission in CFS mode, one is also able to measure the density of empty states. Because the inelastic scattering lengths are short ($\leq 15\text{\AA}$) above the threshold and relatively long ($>100\text{\AA}$) below the threshold,^{47,48} the energy distribution of secondary electrons due to pair creation replicates the conduction band density of states.^{49,50,51}

The Structure and Physical Properties of Wurtzite GaN

Unit cell and Brillouin-Zone

The wurtzite structure has lattice constants a and c describing the hexagonal lattice and a third internal parameter u denoting the fractional separation of the gallium and nitrogen sublattices along the c axis, as shown in Fig. 2.9. The real space structure consists of four interpenetrating hexagonal lattices, or two interpenetrating hexagonal-close-packed (HCP) sublattices, each with one type of atom offset along the c -axis by $5/8$ of the HCP height ($5/8 c$). In the ideal case ⁵², $c/a=(8/3)^{1/2}$ ($=1.633$) and $u=3/8c=|u|$. The actual c/a ratio usually deviates from the theoretical value slightly, for example the HCP

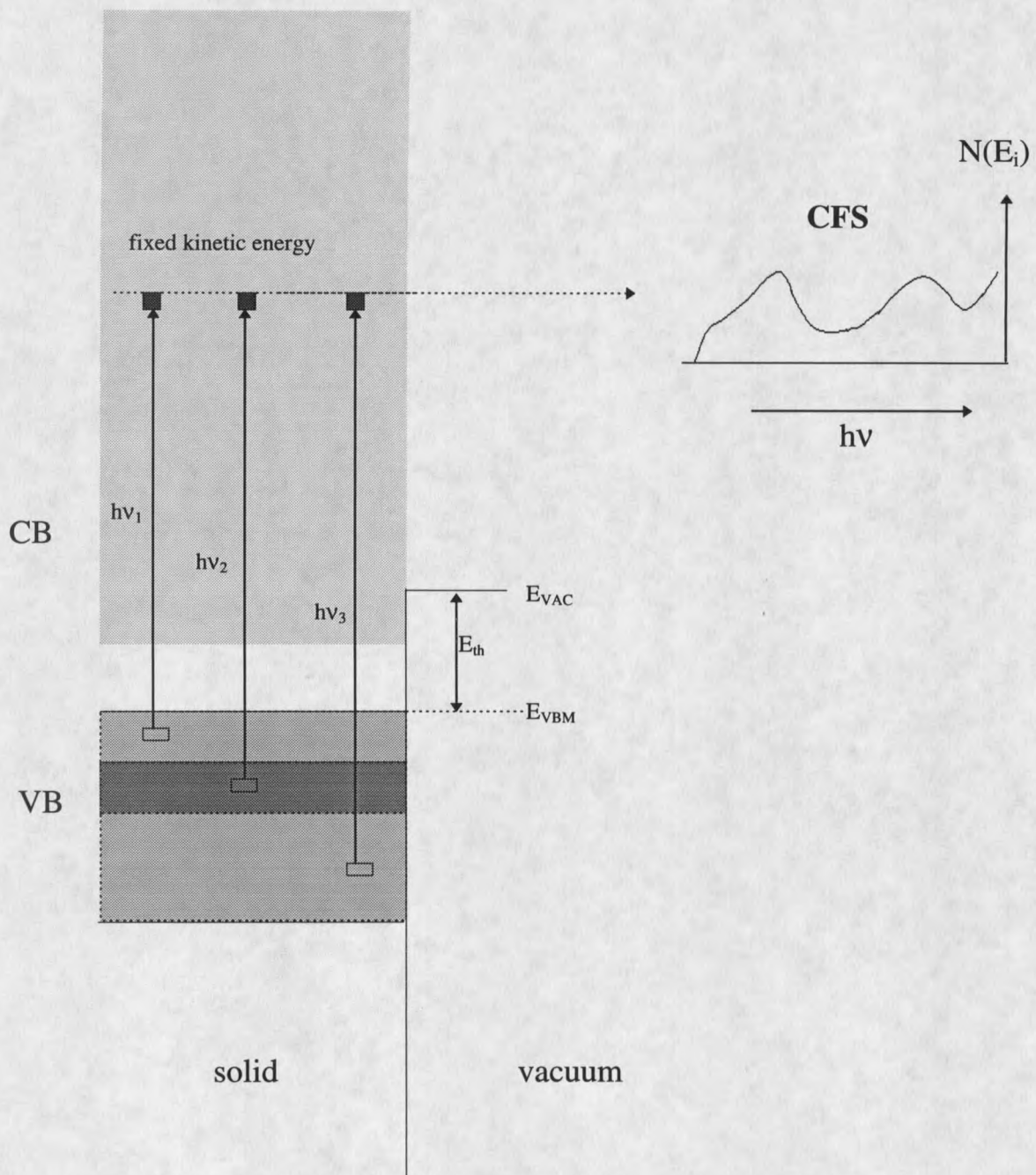


Fig. 2.8 Photoemission spectroscopy in constant final-state-energy spectrum (CFS) mode.

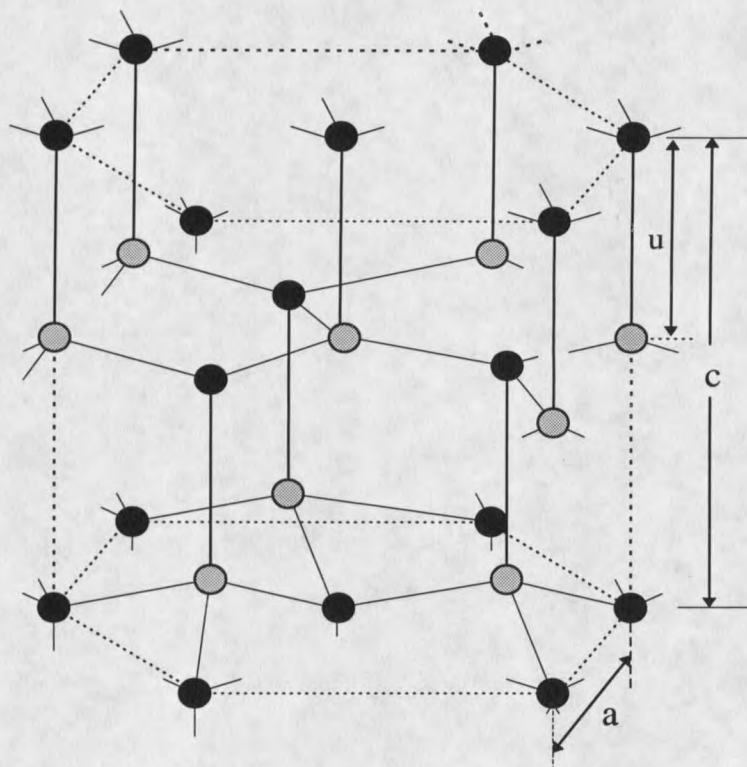


Fig. 2.9 Wurtzite real space structure.

structure of zinc has $c/a=1.85$. Measured values for wurtzite GaN by Marusk et al.⁸ are $a=3.189 \text{ \AA}$, $c=5.185 \text{ \AA}$ and a band gap $E_g = 3.39 \text{ eV}$. The measured internal parameter u is $0.377c$.^{53,54}

HCP structures are usually referenced to four axes with unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ forming the basal plane and $\mathbf{c}$ perpendicular to the basal plane, as shown in Fig. 2.10.

The planes are then denoted by four letter indices $\{h, j, k, l\}$; this is known as the Bravais-Miller method.⁵⁵ Two planes, with their four letter indices, are also shown in Fig. 2.10, with the long dashed lines representing $(10\bar{1}0)$ plane and short dashed lines the

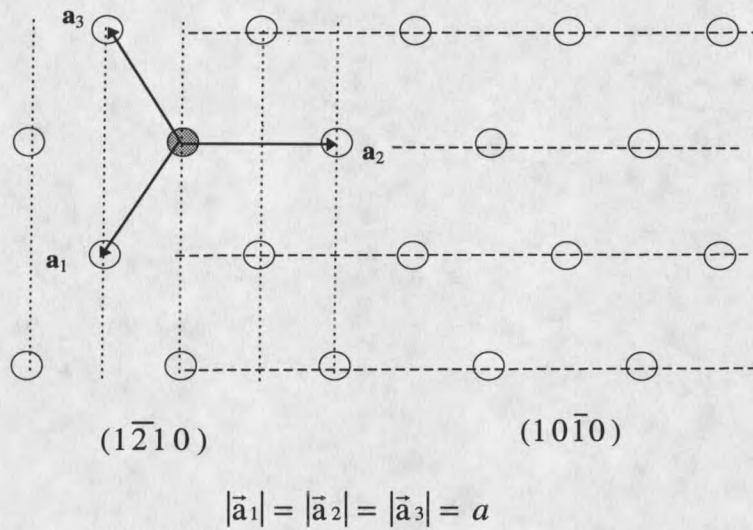


Fig. 2.10 Basal plane formed by unit vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ and two planes represented by the four indices $\{h, j, k, l\}$.

$(1\bar{2}10)$ plane. The indices $\{h, j, k, l\}$ satisfy:

$$h+j+k=0 \quad (2-24)$$

The unit cell for wurtzite GaN is shown in Fig. 2.11. The volume of the unit cell of the simple lattice is thus $\frac{1}{2}\sqrt{3}a^2c$. It contains two gallium and two nitrogen atoms which tells us that there will be eight nitrogen bands, with two 2s bands separated from six 2p bands, and 18 gallium bands (4s, 4p, 3d), with the ten 3d blocks lowest in energy.

The form and size of the Brillouin-zone is determined by the crystal structure only, and can be found easily. The resulting three dimensional Brillouin-zone for the HCP structure is shown in Fig. 2.12.

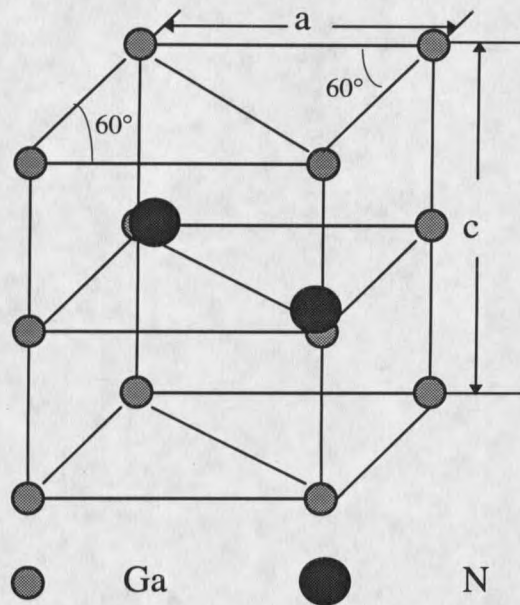


Fig. 2.11 Hexagonal unit cell.

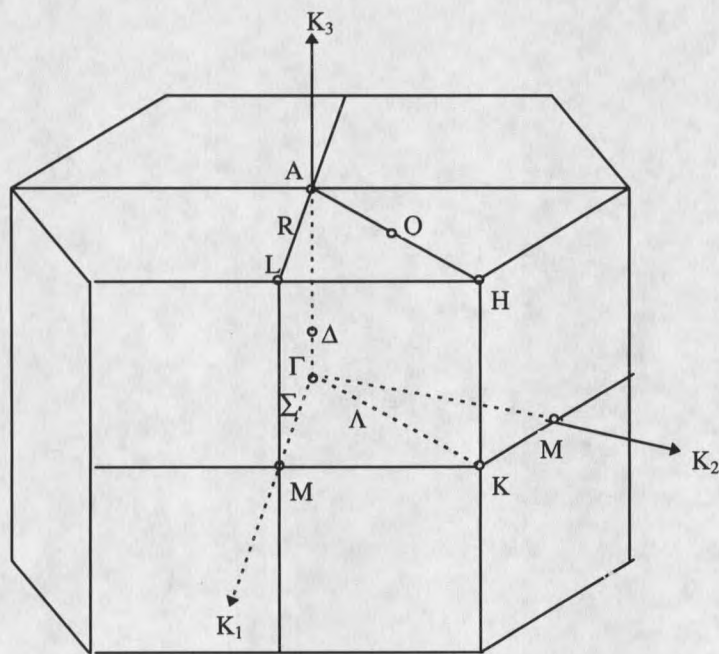


Fig. 2.12 Brillouin-zone of wurtzite structure.

General Physical Properties

The wurtzite GaN structure has two polar planes, planes terminating with either all Ga, the so-called (0001) surface, or all nitrogen, the so-called (000 $\bar{1}$) surface, which is similar to the zinc-blende structure where group III terminated planes are called (111)A and group V terminated planes are called (111)B.

The commonly observed wurtzite GaN conductivity is n-type, typically with a doping level $n > 10^{18} \text{ cm}^{-3}$. Unlike conventional semiconductors, such as silicon, in which the conductivity type can be converted by the addition of appropriate dopants, only compensation occurs in GaN, not conversion. This is believed to be associated with the formation of nitrogen related point defects.⁹

The general physical properties of GaN are compiled in Table 2.1 for convenient references. The relatively high ionization energies of p-type dopants give lower p-type conductivity.

Photoelectron Diffraction Imaging (PDI)

Photoelectron holography is a new and promising technique allowing one to reveal the three-dimensional image of adsorbate or surface atoms on a solid surface. In 1983 J. J. Barton et al. showed that photoelectron diffraction using adsorbate core-levels, measured at a selected angle and an extended photon energy range, can be transformed to give the path-length difference between primary and substrate atom scattered photoelectron waves.⁵⁶ This is the so called angle-resolved photoemission extended fine structure

Table. 2.1 ^{57,58} General physical properties of GaN.

lattice constants: $a=3.189 \text{ \AA}$ $c=5.185 \text{ \AA}$ $u=0.377c=1.955 \text{ \AA}$
band gap(at 300K) 3.4 eV
effective mass: conduction band electrons: $0.2 m_0$ or $0.236 m_0$ ⁵⁹ valence band holes $0.8 m_0$
coefficients of thermal expansion: $5.59 \times 10^{-6}/\text{K}$ (in basal plane) $7.75 \times 10^{-6}/\text{K}$ (along c-axis)
ionicity 35%
Ionization energies: $\text{Si}_\text{N}=0.225 \text{ eV}$ $\text{Mg}_\text{Ga}=0.25$ $\text{Zn}_\text{Ga}=0.34 \text{ eV}$ $\text{Cd}_\text{Ga}=0.55 \text{ eV}$ $\text{Be}_\text{Ga}=0.7 \text{ eV}$ $\text{Fe}_\text{Ga}(E_\text{A}) = 2.5 \text{ eV}$, acceptor ⁶⁰
Thermal conductivity(RT): 1.3 W/cm K
Debye temperature ⁶¹ (at 0K): $\sim 600 \text{ K}$
static dielectric constant: $\epsilon_\text{s} (E_\perp c) \quad 9.5$ $\epsilon_\text{s} (E_\parallel c) \quad 10.4$
melting point ⁶² (normal pressure): 2791 K

(ARPEFS) technique. It has the drawback that all scatterers having the same path-length difference will contribute to the same peak in the Fourier transform. In 1986 A. Szöke⁶³ first suggested that electron microscopy can be achieved by measuring and reconstructing a photoelectron hologram. By 1988, J. J. Barton further expanded the idea by showing that a two-angle photoelectron diffraction pattern gives rise to a photoelectron hologram, with the direct photoemission amplitude being the reference wave and the scattered wave being the object wave,⁶⁴ as depicted in Fig. 1.4 (Chapter 1). Barton's holographic intensity can be obtained from a diffraction pattern as a function of the emission direction $\mathbf{k}$, with fixed k magnitude. The so called single-energy holography can be written as:⁶⁵

$$U(\mathbf{R}) = \left| \sum_j \int A(\mathbf{k}, \mathbf{r}_j) e^{i\mathbf{k}\cdot\mathbf{r}_j} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r}_j)} d\hat{\mathbf{k}} + \sum_j \int A^*(\mathbf{k}, \mathbf{r}_j) e^{-i\mathbf{k}\cdot\mathbf{r}_j} e^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{r}_j)} d\hat{\mathbf{k}} \right|^2 \quad (2-25)$$

From equation (2-25), it can be seen that a large image intensity occurs at $\mathbf{R} = \pm\mathbf{r}_j$. This leads to the problem of twin imaging, i.e. an image at both the actual position $\mathbf{r}_j$ and at the inverted position $-\mathbf{r}_j$.

Single Scattering Case

In 1992, S. Y. Tong introduced a method for spatially resolving images using energy-dependent photoelectron diffraction. The energy-dependent photoelectron diffraction spectra (CIS--Constant Initial State) are first individually Fourier transformed in three-dimensional real space:

$$\phi_{\hat{\mathbf{k}}}(\mathbf{R}) = \int_{k_{\min}}^{k_{\max}} \chi(k\hat{\mathbf{k}}) e^{-ikR} e^{ik\cdot\mathbf{R}} g(k) dk \quad (2-26)$$

where $g(k)$ is a window function which decreases the artificial oscillations at the ends of $\chi(\mathbf{k})$, and $\chi(\mathbf{k})$ is the normalized intensity which is related to photoelectron diffraction intensity $I(\mathbf{k})$ by:

$$I(\mathbf{k}) = (\psi_R + \psi_O) \cdot (\psi_R + \psi_O)^* = |\psi_R|^2 (1 + \chi(\mathbf{k})) \quad (2-27)$$

$$\begin{aligned} \chi(\mathbf{k}) &= I(\mathbf{k}) / |\psi_R|^2 - 1 \\ &= \sum_j A(\mathbf{k}, \mathbf{r}_j) e^{i(kr_j - \mathbf{k} \cdot \mathbf{r}_j)} + \sum_j A^*(\mathbf{k}, \mathbf{r}_j) e^{-i(kr_j - \mathbf{k} \cdot \mathbf{r}_j)} + \\ &\quad \sum_j \sum_l A(\mathbf{k}, \mathbf{r}_j) A^*(\mathbf{k}, \mathbf{r}_l) e^{i[(kr_j - \mathbf{k} \cdot \mathbf{r}_j) - (kr_l - \mathbf{k} \cdot \mathbf{r}_l)]} \end{aligned} \quad (2-28)$$

with $A(\mathbf{k}, \mathbf{r}_j) = F(\hat{\mathbf{r}}_j, k) F^{-1}(\hat{\mathbf{k}}, k) f(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{k}}, k) \frac{e^{-i\gamma_j}}{r_j}$, $F(\hat{\mathbf{r}}_j, k)$ and $F^{-1}(\hat{\mathbf{k}}, k)$ are factors related

to the photoexcitation matrix elements of the emitter and $f(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{k}}, k)$ is the atomic scattering factor⁶⁶ of the scatterer which can be written as (at low kinetic energy):

$$\begin{aligned} f(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{k}}, k) &= f(\cos(\theta), k) \\ &= \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{-i\delta_l} \sin(\delta_l) P_l(\cos(\theta)) \end{aligned} \quad (2-29)$$

where θ is the scattering angle, P_l is a Legendre polynomial, and δ_l the phase shift of the l th partial scattering wave.

Inserting equation (2-28) $\chi(\mathbf{k})$ into equation (2-26), we get:

$$\begin{aligned}\phi_{\hat{\mathbf{k}}}(\mathbf{R}) = & \sum_j \int_{k_{\min}}^{k_{\max}} A(\mathbf{k}, \mathbf{r}_j) e^{-ik[R(1-\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}) - r_j(1-\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_j)]} g(k) dk \\ & + \sum_j \int_{k_{\min}}^{k_{\max}} A^*(\mathbf{k}, \mathbf{r}_j) e^{-ik[R(1-\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}) + r_j(1-\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_j)]} g(k) dk\end{aligned}\quad (2-30)$$

$\phi_{\hat{\mathbf{k}}}(\mathbf{R})$ reaches its maximum amplitude when the phase in the first integral goes to zero,

$$\text{i.e.} \quad R(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{R}}) - r_j(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_j) = 0 \quad (2-31)$$

Since $\hat{\mathbf{k}}$ and $\hat{\mathbf{r}}_j$ are fixed in each CIS inversion $\phi_{\hat{\mathbf{k}}}(\mathbf{R})$, the above maximum amplitude condition can be written as:

$$R = \frac{\text{Const}}{1 - \cos(\hat{\mathbf{k}}, \mathbf{R})} \quad (2-32)$$

This expression gives a parabolic surface with $\mathbf{k}$ as its rotational axis. If the atoms at $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j$ have the same single-scattering path difference, then:

$$R(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{R}}) = r_1(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_1) = r_2(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_2) = \dots = r_j(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{j1}) \quad (2-33)$$

This means that all of the atoms with the same single-scattering path difference can be found on the same parabola, as shown in Fig. 2.13 for atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$. However, when several CIS's along different $\mathbf{k}$ directions are considered, the parabola along all of these different $\mathbf{k}$ directions will intersect at atomic positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j$ and thus will sum to form strong intensity spots, as shown in Fig. 2.13.

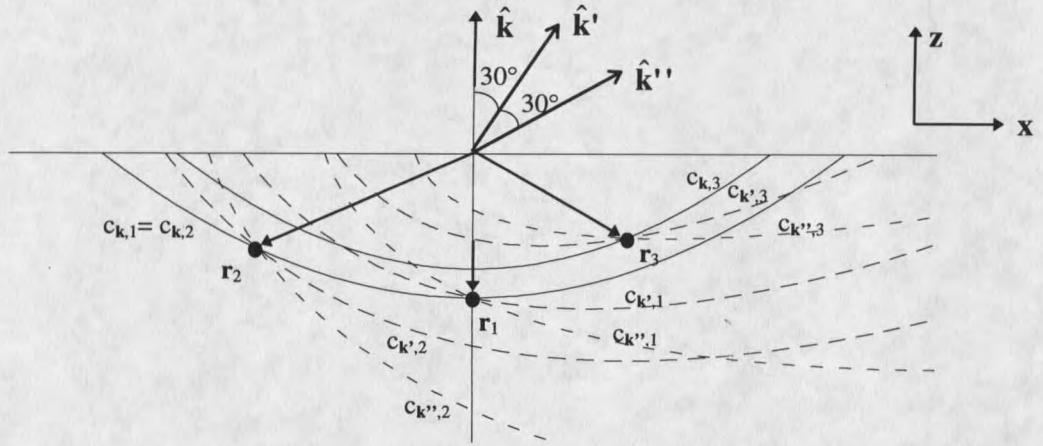


Fig. 2.13 CIS inversion with several CIS's taken along different directions $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$. Atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$ have the same single-scattering path difference with respect to the CIS taken along $\mathbf{k}$ and fall on the same parabola.

With the CIS inversions $\phi_{\hat{\mathbf{k}}}(\mathbf{R})$ by equation (2-26), the real space image function $U(\mathbf{R})$ can be obtained by summing them over either all emission directions (full-window transform) or over a partial range of emission directions (small-window transform²⁵):

$$U(\mathbf{R}) = \left\{ \begin{array}{ll} \left| \sum_{all \hat{\mathbf{k}}} \phi_{\hat{\mathbf{k}}}(\mathbf{R}) \right|^2 & \text{or} \quad \left| \sum_{all \hat{\mathbf{k}}} \phi_{\hat{\mathbf{k}}}(\mathbf{R}) \right| \\ \left| \sum_{\hat{\mathbf{k}} \in \text{Cone}(-\mathbf{R}, w)} \phi_{\hat{\mathbf{k}}}(\mathbf{R}) \right|^2 & \text{or} \quad \left| \sum_{\hat{\mathbf{k}} \in \text{Cone}(-\mathbf{R}, w)} \phi_{\hat{\mathbf{k}}}(\mathbf{R}) \right| \end{array} \right. \quad (2-34a)$$

$$(2-34b)$$

with equation (2-34a) and (2-34b) for the full-window and the small-window (of window width w) respectively.

Effects of Multiple Scattering

We have considered only the single-scattering case up till now, and the path-length difference is simply $\xi = \mathbf{R} - \hat{\mathbf{k}} \cdot \mathbf{R}$. With multiple scattering, for paths that last scattered from atom $\mathbf{r}_\beta$, the normalized diffraction intensity can be written as:²³

$$\chi(\mathbf{k}) = \cdots [A(\mathbf{k}) \frac{e^{ikr_\beta}}{r_\beta} + B(\mathbf{k}) \frac{e^{ikr_\gamma}}{r_\gamma} \frac{e^{ik|\mathbf{r}_\beta - \mathbf{r}_\gamma|}}{|\mathbf{r}_\beta - \mathbf{r}_\gamma|} + \cdots] e^{-ik \cdot \mathbf{r}_\beta} + \cdots \quad (2-35)$$

The first term in equation (2-35) contains the single-scattering path difference $\xi = r_\beta - \hat{\mathbf{k}} \cdot \mathbf{r}_\beta$, while multiple scattering gives a different path difference:

$$\eta = r_\gamma + |\mathbf{r}_\beta - \mathbf{r}_\gamma| - \hat{\mathbf{k}} \cdot \mathbf{r}_\beta \quad (2-36)$$

Substituting equation (2-35) into equation (2-26) will generate an intensity maximum parabola that satisfies:

$$\xi = R - \hat{\mathbf{k}} \cdot \mathbf{R} = \eta = r_\gamma + |\mathbf{r}_\beta - \mathbf{r}_\gamma| - \hat{\mathbf{k}} \cdot \mathbf{r}_\beta \quad (2-37)$$

Solving for R from the above equation gives

$$R = \frac{\eta}{1 - \cos(\hat{\mathbf{k}}, \mathbf{R})} \quad (2-38)$$

$\mathbf{R}$ is independent of $\hat{\mathbf{k}}$ if, and only if:

$$r_\gamma + |\mathbf{r}_\beta - \mathbf{r}_\gamma| = r_\beta \quad \text{and}$$

$$\hat{\mathbf{R}} \parallel \hat{\mathbf{r}}_\beta.$$

With the above two conditions, the solution of equation (2-37) is:

$$\mathbf{R} = \mathbf{r}_\beta.$$

This means that only at $\mathbf{R} = \mathbf{r}_\beta$ will all the parabola intersect for different $\hat{\mathbf{k}}$ directions. Thus multiple scattering will give a general background without intersections at a particular point. This is depicted in Fig. 2.14. In the best case, only two parabola pass through a fixed point, thus the signal to noise ratio by single-event scattering versus multiple scattering will be $(N/2)^2$, with N the number of CIS's used in the transform.

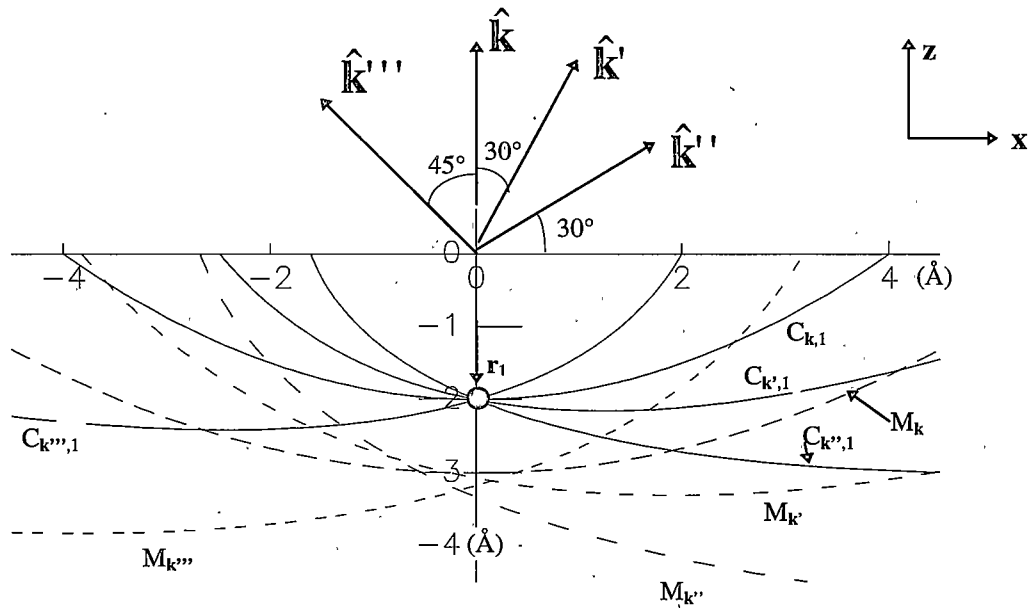


Fig. 2.14 CIS inversion with several CIS's taken along different directions $\mathbf{k}$, $\mathbf{k}'$, $\mathbf{k}''$ and $\mathbf{k}'''$. Single-scattering (solid lines) intersect at atom $\mathbf{r}_1$, while multiple scattering (dashed lines) gives a general background. $|\mathbf{r}_1| = 2 \text{ \AA}$, and a multiple scattering path length $r_\gamma + |\mathbf{r}_\gamma - \mathbf{r}_1| = 4 \text{ \AA}$ are used in the graph.

Metal-Semiconductor Interface

The metal-semiconductor interface is of great importance in semiconductor device technology. When a metal and a semiconductor are brought into contact, the Fermi levels of the two materials are aligned when in thermal equilibrium. In the metal, a charge imbalance Q is screened within a few Ångstroms by the high density of electrons in the metal (usually 10^{23} cm^{-3}).⁶⁷ The potential due to the screened charge is given by:

$$\begin{aligned}\phi(r) &= (Q/r)\exp(-r/r_{\text{TF}}), \\ r_{\text{TF}} &\approx 0.5 (n/a_0^3)^{-1/6}\end{aligned}\tag{2-39}$$

where r_{TF} is the Thomas-Fermi screening length, a_0 is the Bohr radius, and n is the electron density. For example in Cu, $r_{\text{TF}}(\text{Cu}) \approx 0.55 \text{ Å}$. On the other hand, the free carrier concentration in a semiconductor is several orders of magnitude lower and thus a space charge region usually extends hundreds of Angstroms into the surface. Upon deposition of a metal onto a semiconductor surface, some chemical bonds will form and thus the distribution of intrinsic surface states of the metal-free semiconductor surface will be altered. The formation of bonds will lead to charge transfer between the metal and semiconductor. This is described by the formation of a dipole layer of atomic dimensions. The direction of the dipoles is determined by the difference between the metal work function $e\phi$ and the semiconductor electron affinity χ_{SC} , as sketched in Fig. 2.15 which has included an interface region with atomic dimensions explicitly. It was proposed by

Bardeen²⁸ that, if the surface states at the semiconductor surface are not changed by the metal deposition, then surface state densities as low as 10^{12} cm^{-2} will pin the Fermi level for metal coverages in the monolayer range, since such a layer is unable to screen the interface charge. However, this assumption is incorrect since the surface states of clean surfaces are usually strongly affected by the metal deposition.

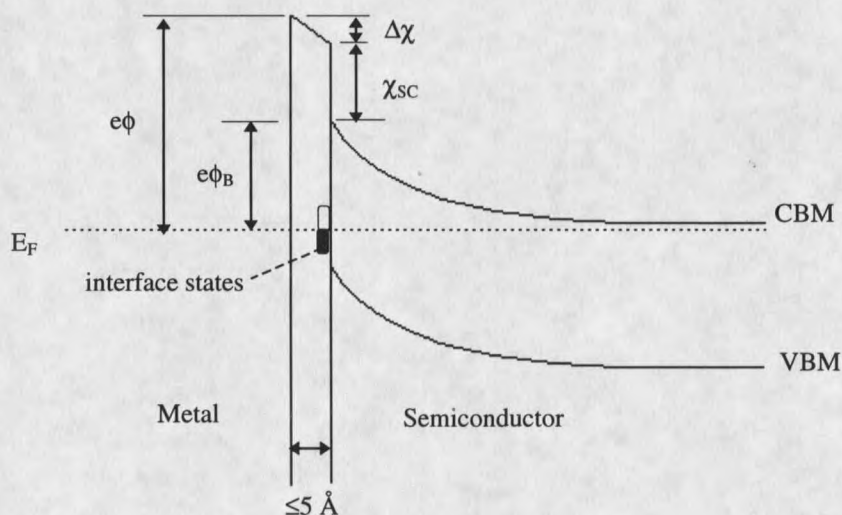


Fig. 2.15 Band diagram of a metal-semiconductor interface. The formation of interface states of sufficient density pins the Fermi level. $e\phi$ is the metal work function, χ_{SC} is the electron affinity of the semiconductor, $\Delta\chi$ is the interface dipole energy, and $e\phi_B$ is the Schottky barrier height.

Taking the interface states into consideration, the total charge balance at the interface now includes the space charge in the semiconductor, the charge in the metal, and

the charge located at the interface. Thus the Schottky barrier height depends sensitively on the nature of these interface states. The origin and nature of these interface states form the central topics of current research into Schottky barrier formation.

Defects Model

The interface defects model was proposed by Wieder⁶⁸, Williams et al.⁶⁹ and Spicer et al.⁷⁰ to explain the Fermi level pinning on metal III-V semiconductor interfaces. According to this model the deposition of a metal leads to the formation of cation or anion vacancies, or antisite defects, i.e. a cation at the interface replaced by an anion, or vice versa. The energy required for defect formation is delivered to the surface by impinging adsorbate atoms. The defect formation thus destroys the charge neutrality nearby, e.g. an As atom on a regular Ga-GaAs site introduces a local positive charge deficiency and acts as a donor-type interface state which readily donates electrons into the conduction band.

A higher density of interface states ($\geq 10^{14} \text{ cm}^{-2}$) is needed to pin the Fermi level with a thick metal overlayer ($>100 \text{ \AA}$) than in the case of sub-monolayer coverage (about 10^{12} cm^{-2}), because the charge in the interface state is compensated not only by the space charge in the semiconductor, but also screened by the free electrons of the now bulk-like metal overlayer. The interface charge density would have to increase from 10^{12} cm^{-2} to $\geq 10^{14} \text{ cm}^{-2}$ to establish a band bending of the order 1 eV.

Work Function Changes Induced by Adsorbates

Adsorption may rearrange the electronic charge within a chemical bond, therefore charge transfer between the adsorbed atom and the substrate would give rise to additional dipoles at the interface. This effect is described by a change on the work function $e\Delta\phi$ due to adsorption, as depicted in Fig. 2.16. For a semiconductor the total work function is described by three terms:

$$e\phi = \chi + eV_s + (E_c - E_F)_{\text{bulk}} \quad (2-40)$$

where χ is the electron affinity of the semiconductor and V_s the surface band bending.

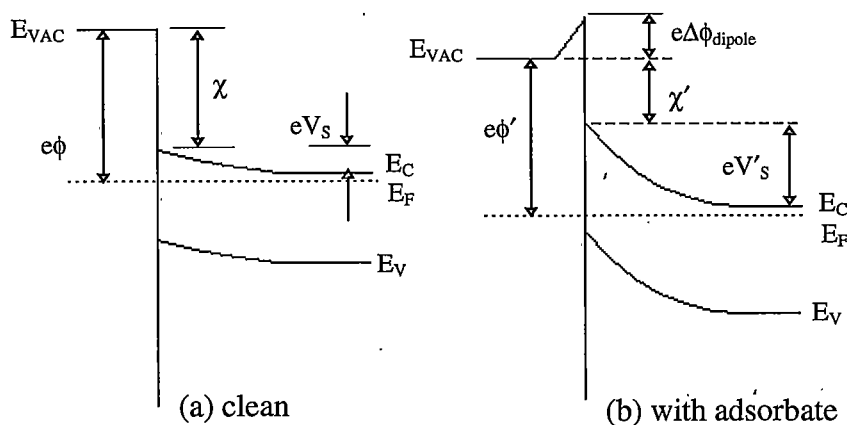


Fig. 2.16 Band diagrams of (a) clean and (b) adsorbate covered semiconductor surfaces. Chemisorption bonding of an adsorbate generally changes the band bending to eV'_s ; charge transfer within the chemisorption bond induces dipoles within the surface and thus changes the work function and electron affinity to $e\phi'$ and χ' , respectively.

The effect of the dipoles caused by adsorption is assumed to change the electron affinity from χ to χ' , and there is an additional band bending change ΔV_s . Thus the total work function change $e\Delta\phi$ of a semiconductor due to adsorption is:

$$e\Delta\phi = \Delta\chi + \Delta V_s \quad (2-41)$$

These two contributions ($e\Delta\phi$ and ΔV_s) can be determined separately by a photoemission experiment. The change of the exact positions of the low kinetic energy edge of the secondaries with respect to the experimentally determined Fermi level E_F gives the absolute value of the work function change $e\Delta\phi$. The high kinetic energy edge of the energy distribution curve (EDC) corresponds to the upper valence band maximum (VBM), and a shift of the VBM relative to the Fermi level indicates a band bending change ΔV_s . Since extrinsic gap states due to adsorption would change the density of state distribution at VBM, and thus make the determination of the VBM onset impossible, band bending changes ΔV_s are usually obtained by shifts in the bulk core-level emission which bend the same way as the valence band at the interface.

Computer Core-Level Voigt Fitting

The full width at half maximum (FWHM) of a core-level line is a complex function of the following contributions:

1. The 'natural' width, or lifetime, of the core-level, $\Delta E = \hbar / \Delta t$, has a Lorentzian functional dependence:

$$L(E) = \frac{1}{(1 + 4(\frac{E - E_L}{\Gamma_L})^2)} \quad (2-42)$$

where Γ_L is the full width at half maximum (FWHM) and E_L the centroid.

2. The resolution or instrumental response function can be represented by a Gaussian function:

$$G(E) = \exp\left\{-4 \ln 2 \left(\frac{E - E_G}{\Gamma_G}\right)^2\right\} \quad (2-43)$$

where Γ_G the FWHM and E_G the centroid.

3. Phonon Broadening ($T > 0K$) can also be represented by a Gaussian function.

The physical representation of the three above FWHM requires a convolution of the Lorentzian and Gaussian functions. Since the convolution of two Gaussians is still a Gaussian, the functional representation of a core-level line-shape is:

$$I(E_G) = \int_{-4\sigma}^{+4\sigma} \exp\left\{-4 \ln(2) \left(\frac{E - E_G}{\Gamma_G}\right)^2\right\} \frac{1}{\left(1 + 4 \left(\frac{E - E_L}{\Gamma_L}\right)^2\right)} dE \quad (2-44)$$

With the Gaussian width representing the instrumental resolution and solid state effects such as phonon and inhomogeneous broadening in the sample.

The assumption that the 'natural' line-width can be represented by Lorentzian is valid for semiconductors and insulators. However, for metals, the creation of long-lived low energy electron-hole pairs near the Fermi level leads to a skewing of the symmetric line-shape toward the low kinetic energy side. Thus we need to replace the Lorentzian line-shape with a Doniach-Sunjjic line-shape:

$$DS(E) = \frac{\text{Gamma}(1-\alpha) \cos\left[\frac{\pi\alpha}{2} + (1-\alpha) \arctan\left(2\frac{E-E_L}{\Gamma_L}\right)\right]}{[(E-E_L)^2 + 4\Gamma_L^2]^{(1-\alpha)/2}} \quad (2-45)$$

where α is the asymmetry parameter, Gamma is the gamma function:

$$\text{Gamma}(\alpha) = \int_0^{\infty} x^{\alpha-1} e^{-x} dx$$

The FWHM is then the result of the convolution : $G \otimes DS$

$$I(E_G) = \int_{-4\sigma}^{+4\sigma} \exp\left\{-4 \ln(2) \left(\frac{E-E_G}{\Gamma_G}\right)^2\right\} \times DS(E) dE \quad (2-46)$$

The surface sensitive core-level photoemission spectra (photoelectron kinetic energies are usually chosen around 45 eV to get the most surface sensitivity) are thus obtained by subtracting a polynomial background, normalizing the count rate to the photon flux read from the tungsten mesh current at the beginning of each scan, and least-square fitting with Gaussian-broadened Lorentzian (Voigt) functions. For core-level emissions like 2p, or 3d, spin-orbital splitting (SOS) gives rise to two components. Each component can be fitted as a Voigt function.

CHAPTER 3

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Synchrotron Radiation Photon Source

As has been discussed in the previous chapters, a continuous photon source is needed to implement studies of the electronic structure of semiconductor surfaces and metal-semiconductor interfaces. Most of the experiments presented in this work (except the ion scattering spectroscopy measurements) are performed at the University of Wisconsin-Madison Aladdin storage ring on the Iowa/Montana beamline.

The synchrotron radiation source can provide a continuous beam of photons spanning the entire energy range from the infrared up to hard x-rays, i.e. photon energies $h\nu$ from 10^{-1} to 10^4 eV or wavelengths λ from 10^5 to 10^{-1} Å. Both electrons and positrons can be used as the charged particles in the orbit of a synchrotron radiation storage ring. However, electrons are preferred due to their smaller mass since the power $P \propto \frac{1}{m^4}$. The typical beam size is about 1.6 mm laterally and 0.3 mm vertically.

The absorption length (reciprocal of optical absorption coefficient) in air is on the order of millimeters and meters for solids and gases, respectively. Therefore a storage ring must be kept under ultra high vacuum ($\sim 10^{-10}$ - 10^{-11} Torr) and all optical components

work in reflection.

Fig. 3.1 shows the schematic layout of synchrotron radiation storage ring. Electrons generated from tungsten filaments are first accelerated to about 108 MeV in the microtron. Then the electrons are injected into the storage ring in 15 bunches with a spatial separation of about 5.9 meters and energized to 800 MeV or 1 GeV. A radio frequency (RF) cavity is placed inside the ring to maintain the electron energy. A series of bending magnets are used to bend the trajectory and to provide the force to make electrons radiate light (any charged particles on a nonlinear trajectory will emit electromagnetic radiation). The high electron velocity thus obtained ($v \approx c$, c is the velocity of light) gives rise to an angular distribution of radiation strongly peaked in the forward direction.⁷¹

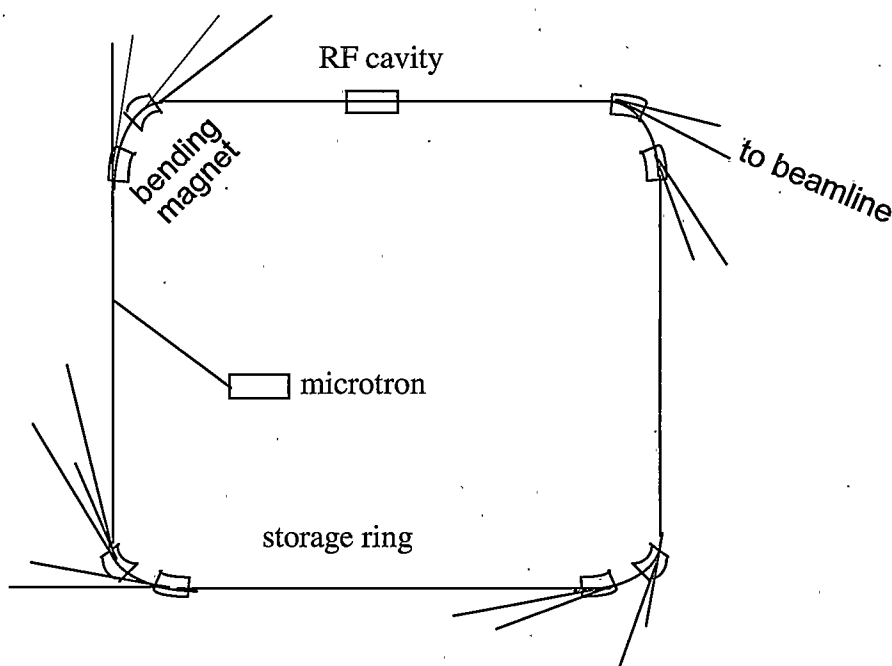


Fig. 3.1 Schematic layout of synchrotron radiation storage ring.

The Combined Seya-ERG Beamline

In order to select a particular energy from the continuous synchrotron radiation source, a monochromator is used. The combined Seya (Seya-Namioka)-ERG (Extended Range Grasshopper) monochromator designed by Dr. Olsen is used on the Iowa/Montana beamline.^{72,73} A schematic optical layout of the Seya-ERG monochromators is shown in Fig. 3.2.

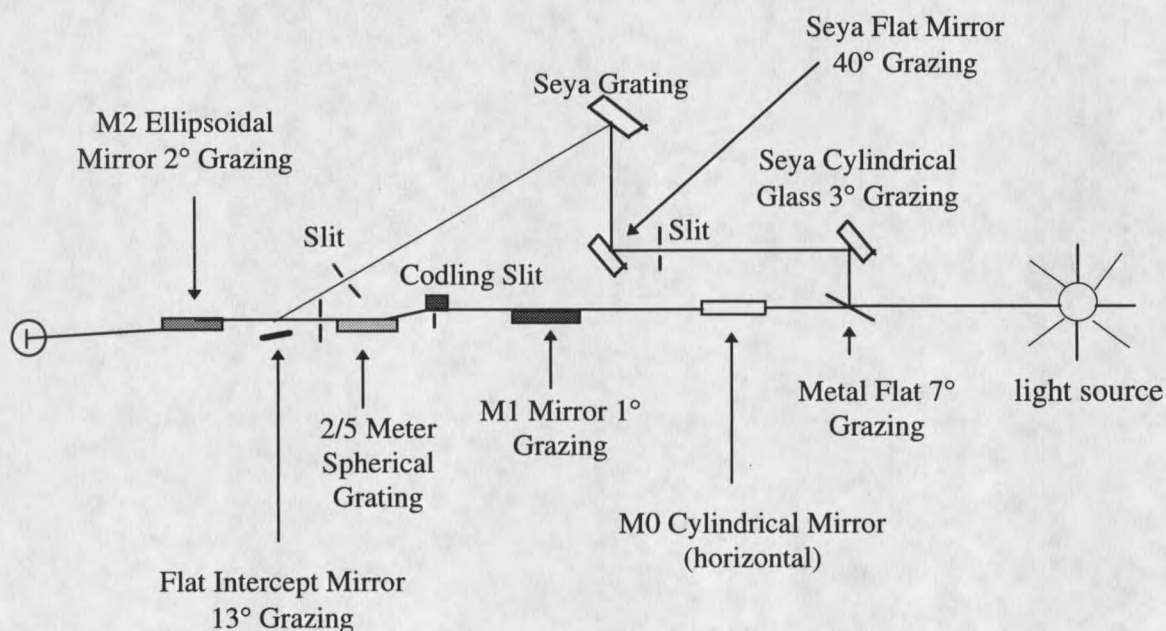


Fig. 3.2 Schematic optical layout of the Seya-ERG monochromators.

The reflectivity R , as a function of grazing angle, can be calculated from the Fresnel equations. When the grazing angle is above a critical angle θ_c , the reflectivity drops dramatically. The critical angle θ_c is: ⁷⁴

$$\theta_c = \sin^{-1} \left[\lambda \left(\frac{e^2 D}{m_0 c^2 \pi} \right)^{1/2} \right] \quad (3-1)$$

where D is the number of electrons per unit volume. From equation (3-1), it is readily seen that at higher photon energy $h\nu$ (or smaller λ), θ_c approaches zero, i.e. grazing angle.

As a practical rule, the reflectivity is small if $\theta \geq \frac{1}{10} \lambda$ (Å). For example: for $h\nu \sim 20$ eV ($\lambda \sim 620$ Å), $\theta \leq 62^\circ$; for $h\nu \sim 100$ eV, $\theta \leq 10^\circ$; and for $h\nu \sim 1$ keV, $\theta \leq 1^\circ$.

So the ultraviolet/x-ray synchrotron radiation spectrum is divided into two parts. One, for $h\nu \sim 30$ eV, $\theta \geq 30^\circ$, normal incidence optics are used. Two, for $h\nu > 30$ eV, grazing incidence optics are used.

Both the normal and grazing incidence monochromators are based on the Rowland circle geometry. ⁷⁴ Fig. 3.3 shows the Rowland circle geometry for a spherical grating. P is the direction perpendicular to the grating surface at the point O . S_i and S_d are the source point and the corresponding focused image point of the diffracted beam, at distance r_i and r_d from the grating point O . θ_i and θ_d are the incidence and diffraction angles. The grating theory shows that if S_i lies on the circle shown in the figure, then S_d also lies on the same circle. This circle, known as the Rowland circle, has center C , is in a plane perpendicular to the grating grooves at the point O , and is in contact with the grating surface. Its radius is $R_c / 2$, where R_c is the radius of curvature of the reflecting surface of the grating.

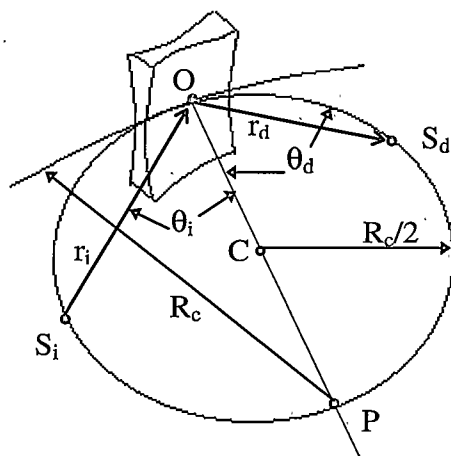


Fig. 3.3 Rowland circle geometry for spherical grating.

The Seya-Namioka (Seya) monochromator is one kind of normal incidence monochromator. The monochromator contains a concave spherical grating. It provides a good compromise between flux and resolution. The Seya monochromator used on the Iowa/Montana beamline has four gratings, providing photons with energy from 5 to 60 eV which is optimal for valence band measurements. The resolution is less than 10 meV for $h\nu < 15$ eV and less than 100 meV for $15 \text{ eV} < h\nu < 50$ eV (at entrance and exit slit size of $200 \mu\text{m}$).

For grazing incidence, the ERG monochromator is used. The 2 meter and 5 meter ERGs provide photons with energy from 37.5-300 eV and 250-1200 eV, respectively. Typically, the photon source resolutions for the 2 meter ERG are about 45 meV and 180 meV at $h\nu = 100$ and 200 eV. The typical 5 meter ERG resolutions are about 0.121 eV,

0.335 eV and 0.857 eV at $h\nu = 300, 500,$ and 800 eV (at both entrance and exit slit sizes of $10\text{ }\mu\text{m}$).

Fig. 3.4 shows the schematic geometry of the grazing angle Grasshopper monochromator with a fixed exit slit. The operation of this kind of monochromator is based on the coordinated motion of the focusing mirror m_1 , the entrance-slit mirror m_2 , and the grating g . The motion results in a rotation of the Rowland circle (rc to rc' in Fig. 3.7) around the exit slit, which changes the center of Rowland circle from C to C' .

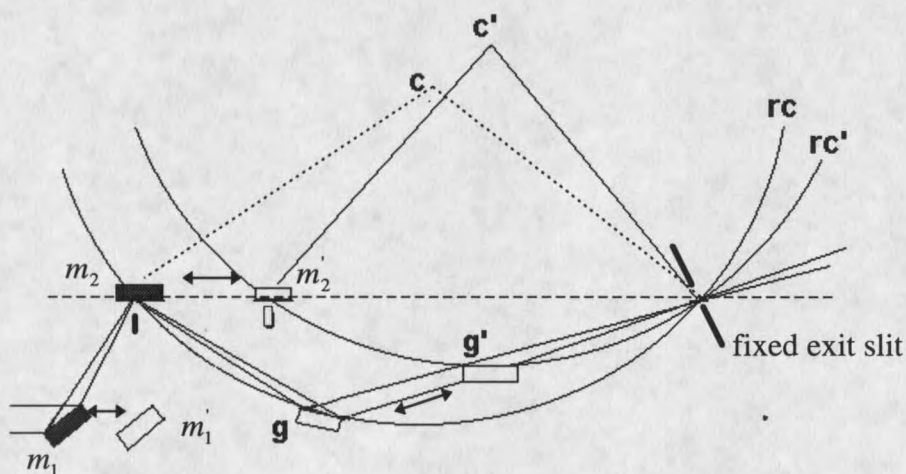


Fig. 3.4 Schematic geometry of grazing angle Grasshopper monochromator with a fixed exit slit.

Vacuum Chambers and Measurement Geometry

The vacuum system is shown schematically in Fig. 3.5. It consists of three stages.

The first stage is the introduction chamber ($\sim 5 \times 10^{-7}$ Torr) for loading the sample from the air (loadlock). The second stage is the intermediate chamber ($\sim 6 \times 10^{-10}$ Torr), which is used for sample preparation. The third stage is the main analysis chamber, which connects to the monochromator by the angle valve #3. The gate valves #1 and #2 isolate the passage between the above three chambers. The transfer manipulator (#4) is used to transfer the sample between the first and second stage, and the transfer manipulator (#5) is used to transfer the sample between the second and third stage.

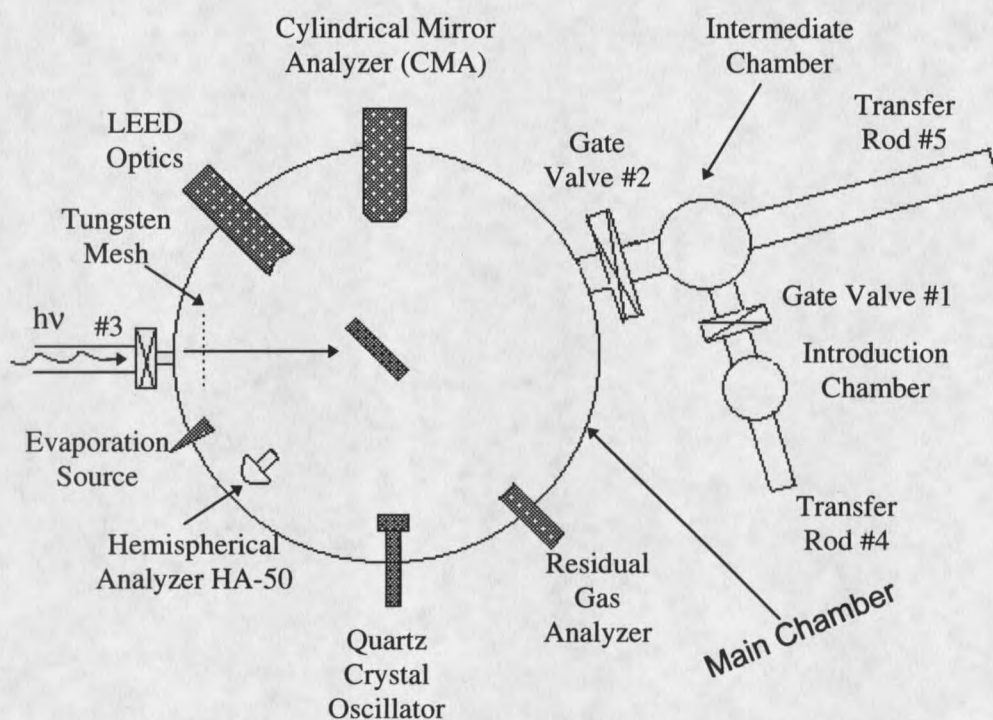


Fig. 3.5 Schematic layout of vacuum system.

Fig. 3.6 shows the schematic layout of the measurement geometry. The sample manipulator has three translational motions (x , y , z) and two rotational motions, with ϕ rotating about the z axis and φ rotating about the sample normal $\hat{n}$. Point O is the point at which the incident beam hits the sample, y' is the zero axis of the HA-50 goniometer (when $\psi = 0$, see Fig. 3.6), and $\hat{t}$ is the sample horizontal axis across the sample surface. The HA-50 analyzer mounted on the goniometer is attached vertically on the turntable. The goniometer can rotate horizontally in θ or vertically in ψ . Measurements are usually made with fixed ψ (0°) and ϕ (62.5°), while rotating angle θ by the HA-50 goniometer and φ by the sample manipulator.

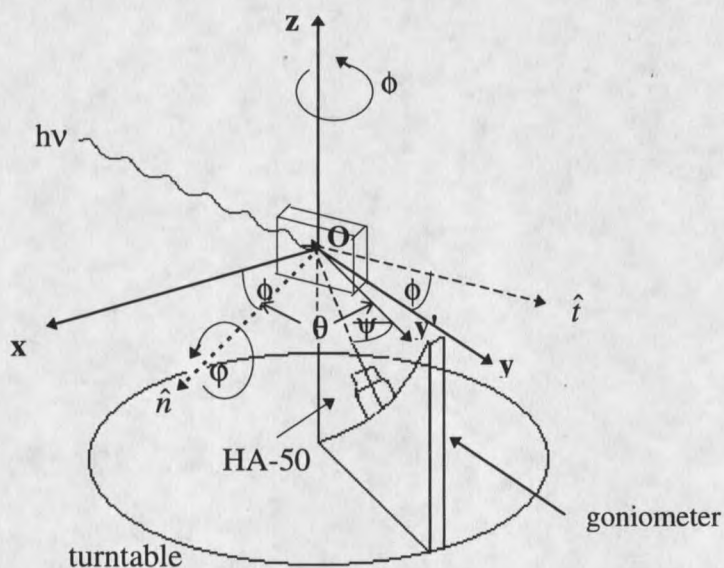


Fig. 3.6 Schematic layout of the measurement geometry.

Electron Energy Analyzer

The hemispherical analyzer HA-50 (Fig. 3.5) is made by Vacuum Science Workshop (VSW) and is used for angle-resolved photoemission measurements. The analyzer is drawn schematically in Fig. 3.7. It consists of two concentric hemispheres, with inner and outer hemisphere radius of R_{in} and R_{out} , respectively. For transmission of electrons with initial energy E_0 along a path with $R_0 = (R_{in} + R_{out})/2$, the potential of the outer hemisphere has to be $V_{out} = E_0 \{3 - 2(R_0/R_{out})\}$ and the inner hemisphere potential $V_{in} = E_0 \{3 - 2(R_0/R_{in})\}$.⁴²

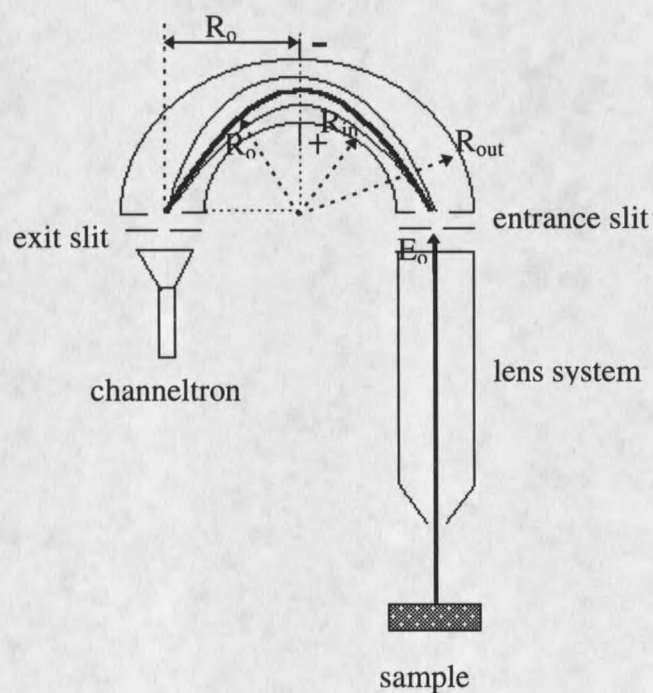


Fig. 3.7 Schematic layout of hemispherical analyzer.

In Fig. 3.7, electrons emitted from the sample are accelerated or retarded by the ramping voltage on the lens system to the pass energy.^a The electrons are then deflected through the hemisphere to the exit slit, where they strike the channeltron. The channeltron has a conelike opening and a continuous tube of high resistivity, semiconducting glass with a high secondary emission coefficient. A high electric field is applied along the tube, and incident electrons create a shower of secondary electrons which in turn hit the tube walls and create further secondaries. A gain of 10^6 to 10^8 can be achieved with the output taken through an amplifier-rate meter system.

The HA-50 has a half acceptance angle of about 2° . The mean radius of the hemisphere is 50 mm. The resolving power $E/\Delta E$ is about 100.

The double-pass cylindrical mirror analyzer (CMA) is used for angle-integrated photoemission measurements. Interested readers can find detailed descriptions of the CMA analyzer from references.^{75,76}

^a A pre-retarding device offers a simple way for improving the resolution of the analyzer. This is because the resolution of the analyzer is a fixed percentage (say 1%) of the transmission energy. Hence, the separation of electron energies becomes better at smaller transmission energies. If electrons with initial energies around 1000 eV are decelerated down to 100 eV by a variable retarding potential between the sample and the entrance slit of the analyzer, then an analyzer resolution of 1% enables the separation of lines with an energy difference of only 1.0 eV, while without preretardation the resolution would have been 10 eV.

CHAPTER 4

VALENCE BAND MAPPING OF WURTZITE GAN

Angle-resolved photoemission (ARP), together with the use of a synchrotron radiation source, provides a very powerful tool to study the electronic band structures of solids. This technique has been widely used since the late 70's (see Chapter 2). In recent years, great effort and significant progress has been made in the crystal growth of wide band gap semiconductors ($E_g > 2.3$ eV). Many applications are dependent on the fabrication of high-temperature, high power and high frequency optoelectronic devices, such as high-brightness GaN/InGaN blue light emitting diodes (LEDs).⁷⁷ In spite of the rapid technological advances which have been made in developing these wide-band-gap semiconductor-based devices in the past 3-4 years, the fundamental understanding of these materials is still lacking and is urgently needed in order to direct and further advance the technological aspects of various applications.

Although some theoretical and experimental work on GaN can be found in the literature, the fundamental understanding of the electronic structures of GaN is still in its infancy. This work reports experimental measurements of the valence band structure of wurtzite GaN along the $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Lambda K$ symmetry lines of the Brillouin zone (See Fig. 2.11 for the Brillouin zone of the wurtzite structure), obtained by normal and off-normal ARP on MBE grown GaN(0001) films. Our results are compared to the calculated

band structures.⁴³

From Fig. 2.2 (Chapter 2) one can see that while parallel momentum $k_{\parallel}$ is conserved in the reduced zone scheme (direct transition) by the furnishing of crystal momentum in units of reciprocal lattice vectors, the perpendicular momentum $k_{\perp}$ is not conserved across the crystal surface due to the potential barrier at the surface. In order to obtain the initial-state energy dispersions within the crystal, the final-state energy dispersions need to be known. The free-electron final state approximation is a simple model which is often used in obtaining the valence band dispersions of conventional III-V compounds. It has proved to be a very successful model by many workers.⁷⁸ The simple free-electron final state model is also found to work quite well for wurtzite GaN with photon energies above 24 eV. This is manifested by the clear dispersions of the initial state energies, with photon energy, in the normal emission data.

Using crystal lattice constants $a = 3.189 \text{ \AA}$ and $c = 5.185 \text{ \AA}$ (see Table 2.1), the Brillouin zone dimensions are: $\Gamma\Delta A = \pi/c = 0.606 \text{ \AA}^{-1}$, $\Gamma\Sigma M = \pi/(a \cdot \cos(30^\circ)) = 1.137 \text{ \AA}^{-1}$ and $\Gamma\Lambda K = \pi/(a \cdot \cos^2(30^\circ)) = 1.313 \text{ \AA}^{-1}$.

By employing the free-electron final state approximation, normal emission measurements give rise to energy dispersions for the (upper) valence band along the $\Gamma\Delta A$ symmetry line. The results are in good agreement with the calculated band. Off-normal emission measurements are also performed in order to obtain the dispersion along the $\Gamma\Sigma M$ and $\Gamma\Lambda K$ symmetry lines. The dispersions along the $\Gamma\Sigma M$ and $\Gamma\Lambda K$ are obtained by changing both the photon energy and emission angle so that the perpendicular momentum is kept at the center of the Brillouin zone (reduced-zone scheme), while the parallel

momentum is scanned along a high symmetry line in the Brillouin zone.⁷⁹ Critical point energies at Γ , A, M, K are found and compared to various calculated values. Note that the free-electron final state approximation will deviate from the actual final states most at the Brillouin zone boundaries (see Fig. 2.1 in Chapter 2), thus will give a larger error at these critical points. Nevertheless, there is an overall agreement of the valence band with the calculated bands along all three symmetry lines of the Brillouin zone. See Figures 4.7 and 4.14 and the corresponding text below for detail.

Sample Preparation

The greatest concern for measuring electronic structures by photoemission is sample quality and surface preparation. In the present studies, the samples were obtained from outside growers and the surface was prepared after mounting in the analysis chamber. More than ten wafers were cleaned and eight different MBE grown wafers, provided by SVT Associates, were measured. While some differences were found, the observed inter-band transition features all yielded essentially the same band structure. Several cleaning procedures were used: 1) annealing in ultra high vacuum (UHV) up to $\sim 850^\circ\text{C}$; 2) covering with a thick layer of Ga metal which was then desorbed up to $\sim 850^\circ\text{C}$; and 3) annealing in Ga flux (Ga source temperature held at $\sim 800^\circ\text{C}$) at a "working temperature" of around 650°C for 10 minutes, followed by gradually decreasing the temperature over about 10 minutes after the Ga flux is stopped. Spectra from several different samples are shown in Fig. 4.1 by the above three different surface preparation

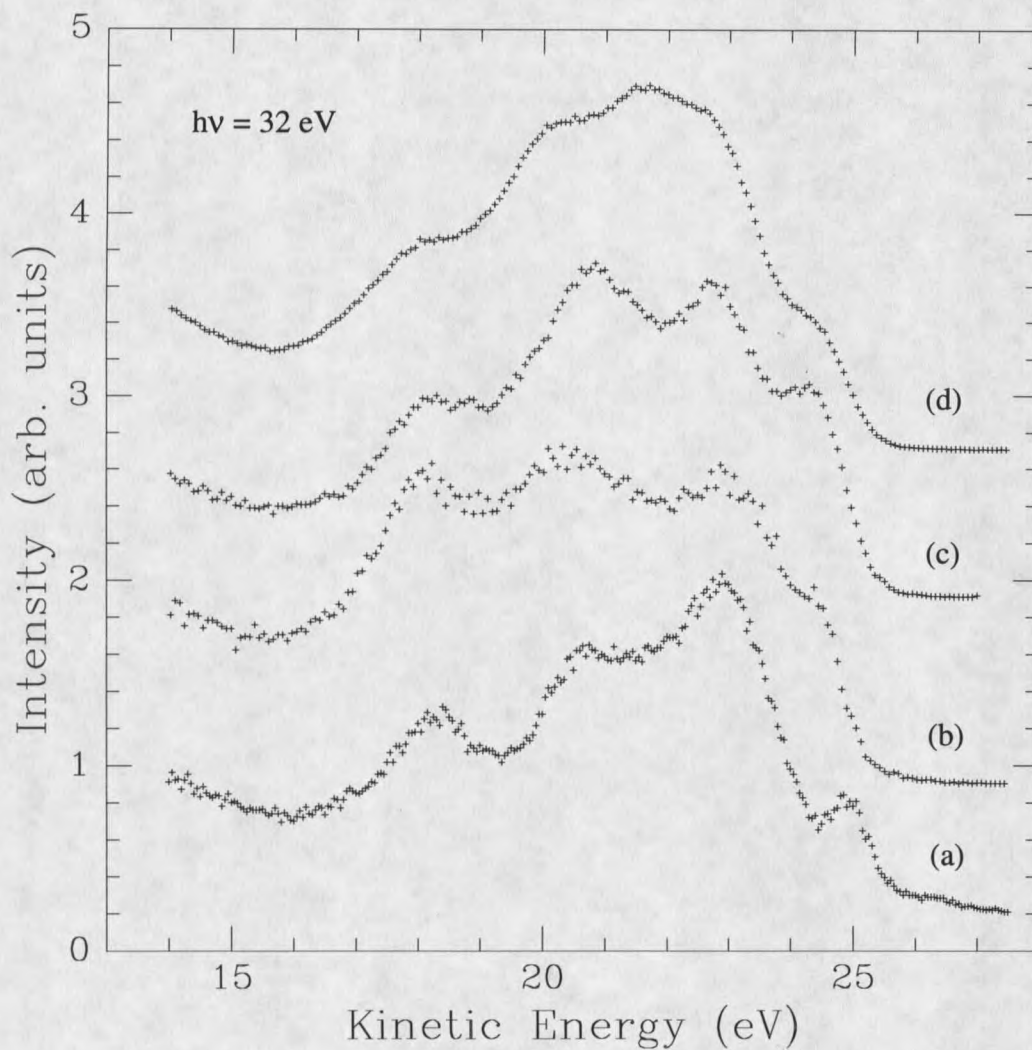


Fig. 4.1 Comparison of the valence band structure obtained from several samples using different surface cleaning procedures. (a) annealing in Ga flux at a "working temperature" of around 650°C for 10 minutes, followed by gradually decreasing the temperature over about 10 minutes after the Ga flux is stopped, (b) covering with a thick layer of Ga metal which was then desorbed up to ~850°C, and (c), (d) annealing in UHV up to ~850°C. (a) to (c) were taken with HA50 in angle-resolved mode while (d) was taken with CMA in angle-integrated mode.

procedures. Fig. 4.1(a) is cleaned by procedure 3, Fig. 4.1(b) by procedure 2, and Fig. 4.1(c),(d) by procedure 1. Fig. 4.1(a)-(c) were taken with HA50 in angle-resolved mode while Fig. 4.1(d) was taken with CMA in angle-integrated mode. For all the three cleaning procedures, carbon was almost always easily removed but oxygen was more difficult to completely remove. The surface obtained by cleaning procedure 3 (under Ga flux) showed no C 1s or O 1s signals as shown in Fig. 4.2 and Fig. 4.3, while the other cleaning procedures yielded no C 1s signal but a small oxygen signal.

The samples (MBE grown GaN film about $1\mu\text{m}$ thick on a sapphire (0001) substrate) were heated by mounting them on a Ta strip, or by pressing them against a silicon wafer, which was then resistively heated. Using a Si wafer was preferred, as well as metallizing the back side of the sapphire. The latter improved the reliability of the optical pyrometer temperature reading. The electrical contact between the sample and the serpentine shaped Ta foil was made by a little indium (In) solder sputtered onto the sample. In the end, however, no need for the In solder was found. Most measured samples were heavily doped n-type ($n^+ \sim 1-2 \times 10^{19} \text{ cm}^{-3}$); a few were p-type. Some solders containing tin (Sn) were tried, but it was found that tin quickly covered the surface when heated while In migration was not observed.

The spectra were measured at the University of Wisconsin-Madison 240-MeV storage ring Synchrotron Radiation Center (SRC) on the Iowa/Montana beam line. The flexibility of the beam-line was very important in this study. The near normal incidence monochromator (SEYA) was used for the photon energy from 10 to 37 eV and the low energy Extended Range Grasshopper (ERG 2-meter) monochromator from 37.5 to 240

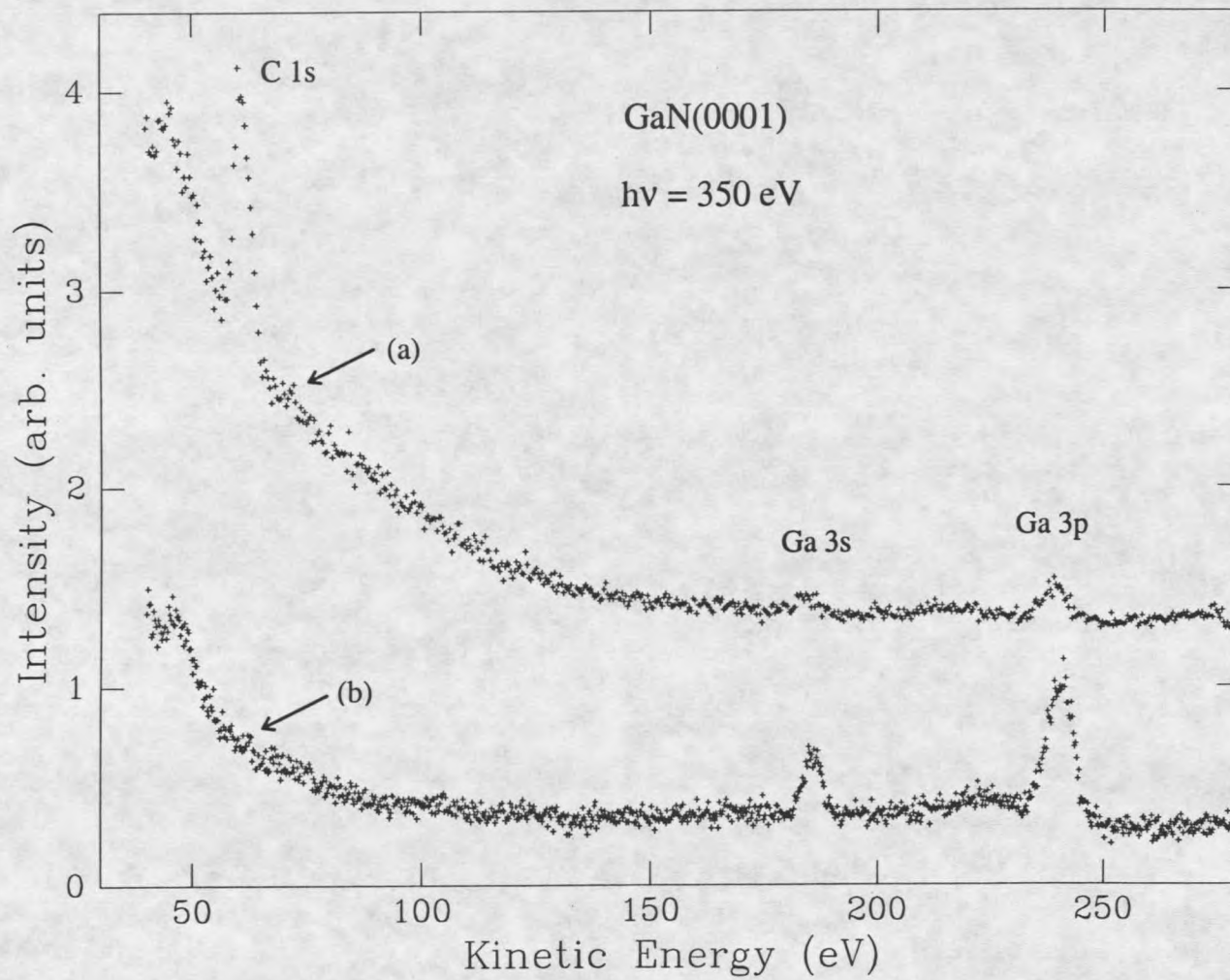


Fig. 4.2 EDC overview scan taken at $h\nu = 350$ eV
(a) before and (b) after cleaning procedures.

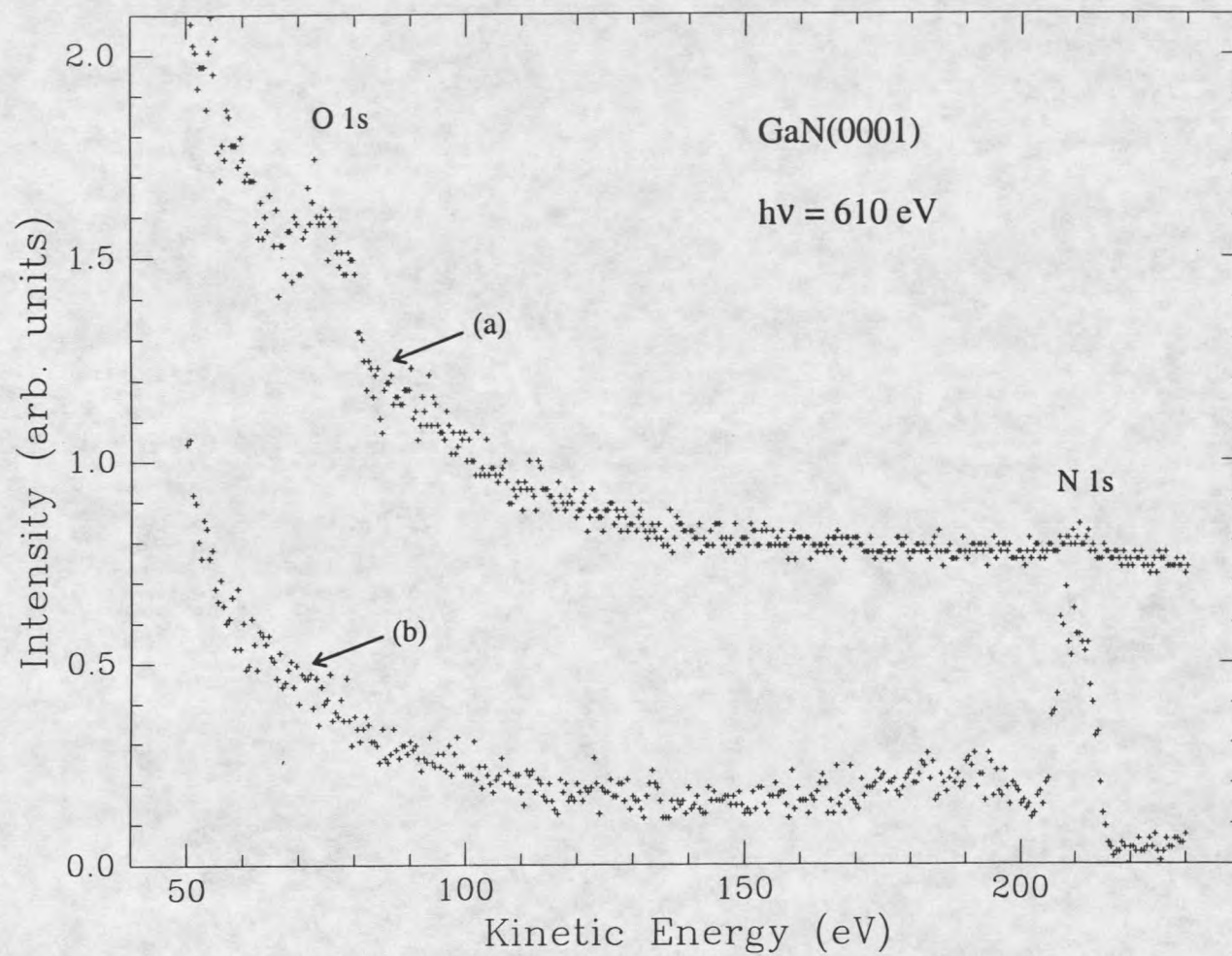


Fig. 4.3 EDC overview scan taken at $h\nu = 610$ eV
(a) before and (b) after cleaning procedures.

eV. This is an optimal combination for electronic structure studies. The high energy ERG grating (ERG 5-meter) was used for photon energies above 300 eV allowing data collection for the 1s core-levels of carbon, nitrogen, and oxygen, which were used for monitoring the sample cleanness even though the signal intensity and resolution are modest. The samples were also characterized by low energy electron diffraction (LEED) in the analysis chamber. The clean surface showed a clear hexagonal 1×1 LEED pattern.

The angle and energy resolved spectra were obtained with an electrostatic 50 mm hemispherical analyzer (VSW model HA50, see chapter 3). The overall instrumental energy resolution was ≤ 0.1 eV for $h\nu \leq 36$ eV and increased up to ~ 0.15 eV at $h\nu = 74$ eV. The angular acceptance of HA50 was about 2° . The analysis chamber contained a Φ (PHI) double pass cylindrical analyzer which was used for some measurements, particularly for $h\nu > 400$ eV.

Normal Emission

A typical EDC (energy distribution curve) spectrum, including the upper valence band down to the Ga 3d core level emission, taken at photon energy 62.5 eV is shown in Fig. 4.4 at normal emission with the VBM (valence band maximum) chosen as the reference level. The upper valence band, with initial state energy above -8 eV, consists of three major peaks which corresponds to Ga 4s-N 2p (E_i about -6 eV) and Ga 4p-N 2p (E_i about -2 eV) derived states. The Ga 3d emission is located at -17.9 eV. A relatively broad N 2s emission is observed at 3.04 eV above the Ga 3d emission, as shown in Fig. 4.5 by

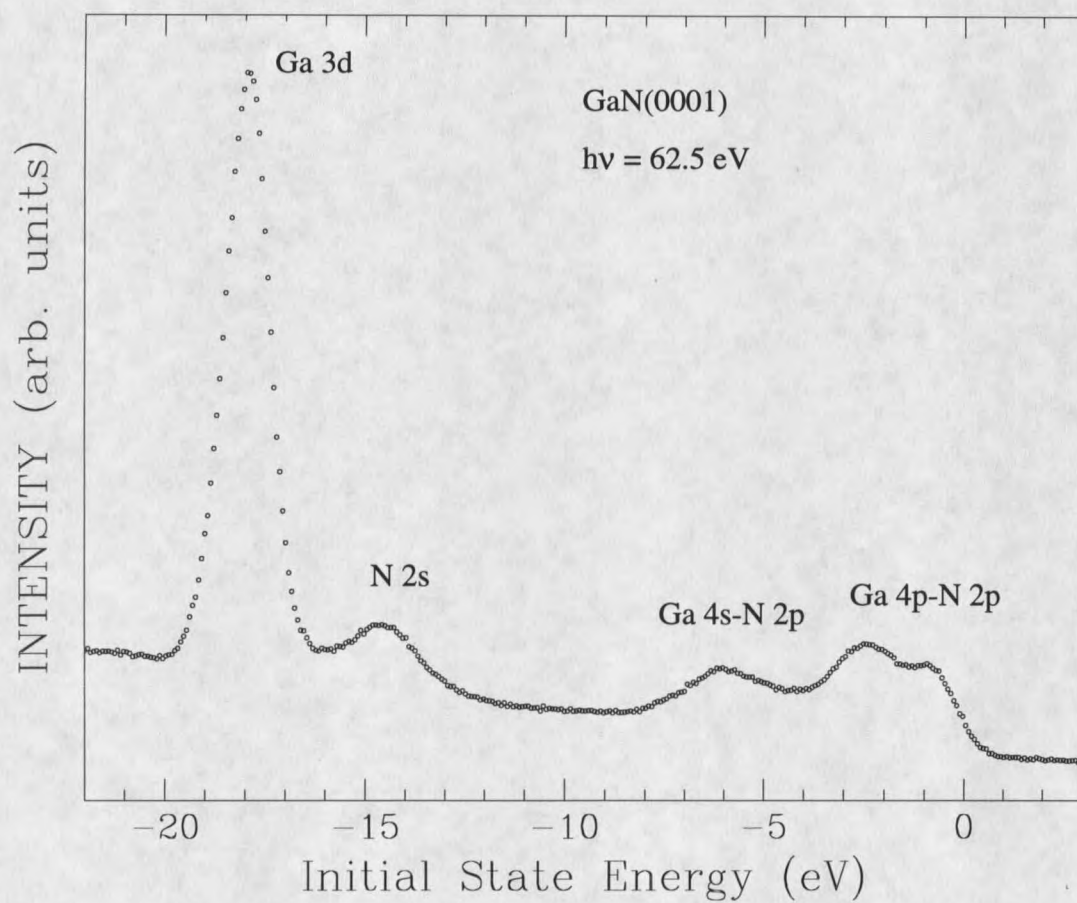


Fig. 4.4 A typical EDC spectrum including the upper valence band down to the Ga 3d core level emission taken at photon energy of 62.5 eV at normal emission. The VBM is chosen as the reference level.

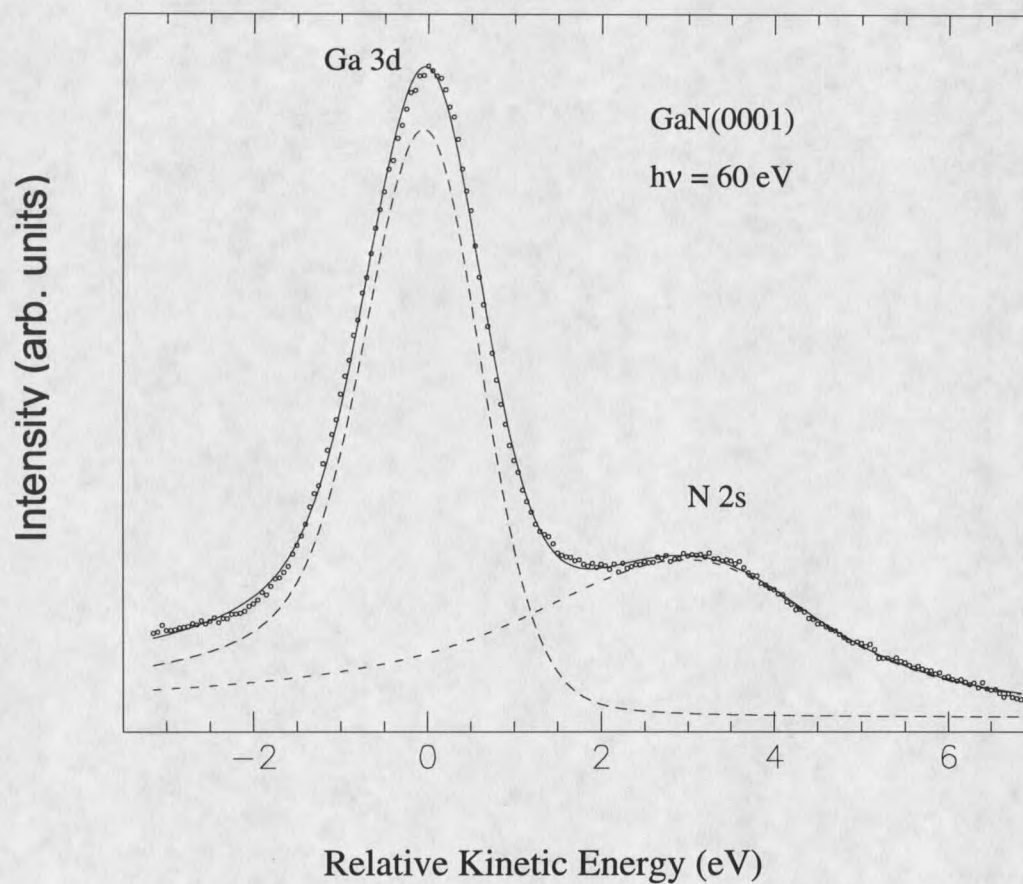


Fig. 4.5 Voigt fitting of the Ga 3d and N 2s core-levels. A relatively broad N 2s emission is observed which is located 3.04 eV above the Ga 3d emission. The EDC is taken at $h\nu = 60$ eV and the kinetic energy shown is relative to the Ga 3d emission.

Voigt (Lorentzian convoluted with Gaussian) fitting of the two emissions at $h\nu = 60$ eV.

Fig. 4.6(a) and 4.6(b) show the normal emission spectra ($\theta = 0^\circ$) taken with two monochromators. Fig. 4.6(a) was taken with SEYA in the photon energy range $21 \leq h\nu \leq 36$ eV; and Fig. 4.6(b) was taken with ERG in the photon energy range $37.5 \leq h\nu \leq 74$ eV. This corresponds to probing the Brillouin zone along the $\Gamma\Delta A$ symmetry line with wave-numbers in the range 2.7 to $4.3 \text{ \AA}^{-1}$. Similar normal emission experiments were repeated several times and the results were reproducible.

Normal emission spectra with photon energies in the range $21 \leq h\nu \leq 74$ eV were chosen for the "band-mapping" of wurtzite GaN. At higher photon energies (>74 eV), the upper valence band derived from Ga 4s -N 2p (see Fig. 4.6(b)) tends to die out at higher final states. This is due to the smaller cross section for initial states with low angular momentum. On the other hand, at lower photon energies (< 21 eV), the nearly free electron final state approximation is no longer valid. This is because the crystal potential is no longer a weak perturbation with lower photon energies reaching lower final states.

With the direct transition model and the free-electron parabola final state approximation, the photoelectron momentum inside the crystal is related to the experimental parameters including photon energy $h\nu$, initial state energy E_i referenced to VBM, emission angle θ , and photo-threshold Φ_{th} by : ⁷⁹

$$\hbar k_{\parallel} = (2mE_k)^{1/2} \sin \theta = [2m(E_i + h\nu - e\Phi_{th})]^{1/2} \sin \theta \quad (4-1a)$$

$$\hbar k_{\perp} = [2m(E_k \cos^2 \theta - V_0)]^{1/2} = \{2m[(E_i + h\nu - e\Phi_{th}) \cos^2 \theta - V_0]\}^{1/2} \quad (4-1b)$$

where V_0 is the inner potential, $V_0 = E_0 - e\Phi_{th}$.

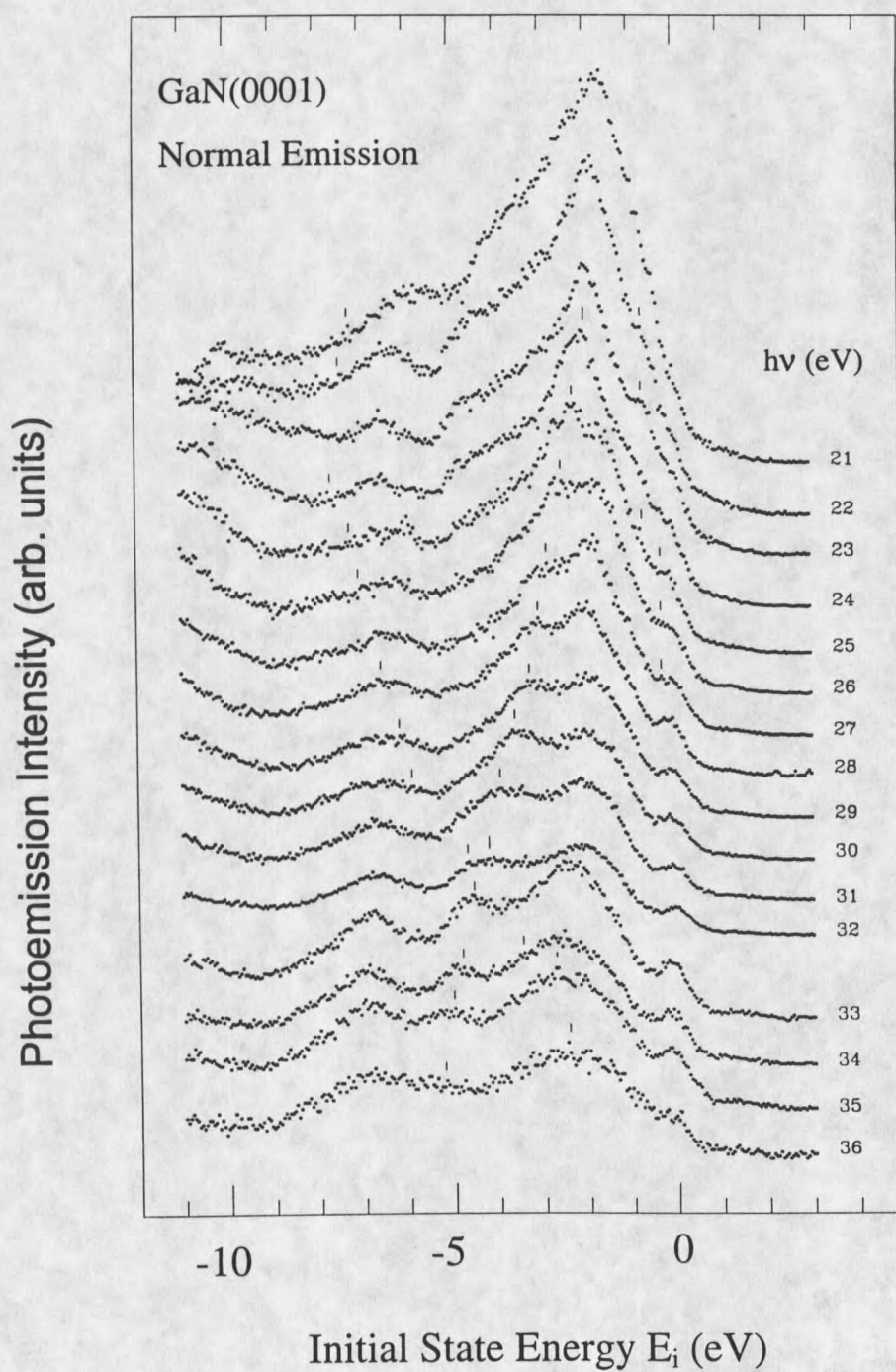


Fig. 4.6(a) Normal emission spectra ($\theta = 0^\circ$) taken with SEYA monochromator in the photon energy range of $21 \leq h\nu \leq 36$ eV.

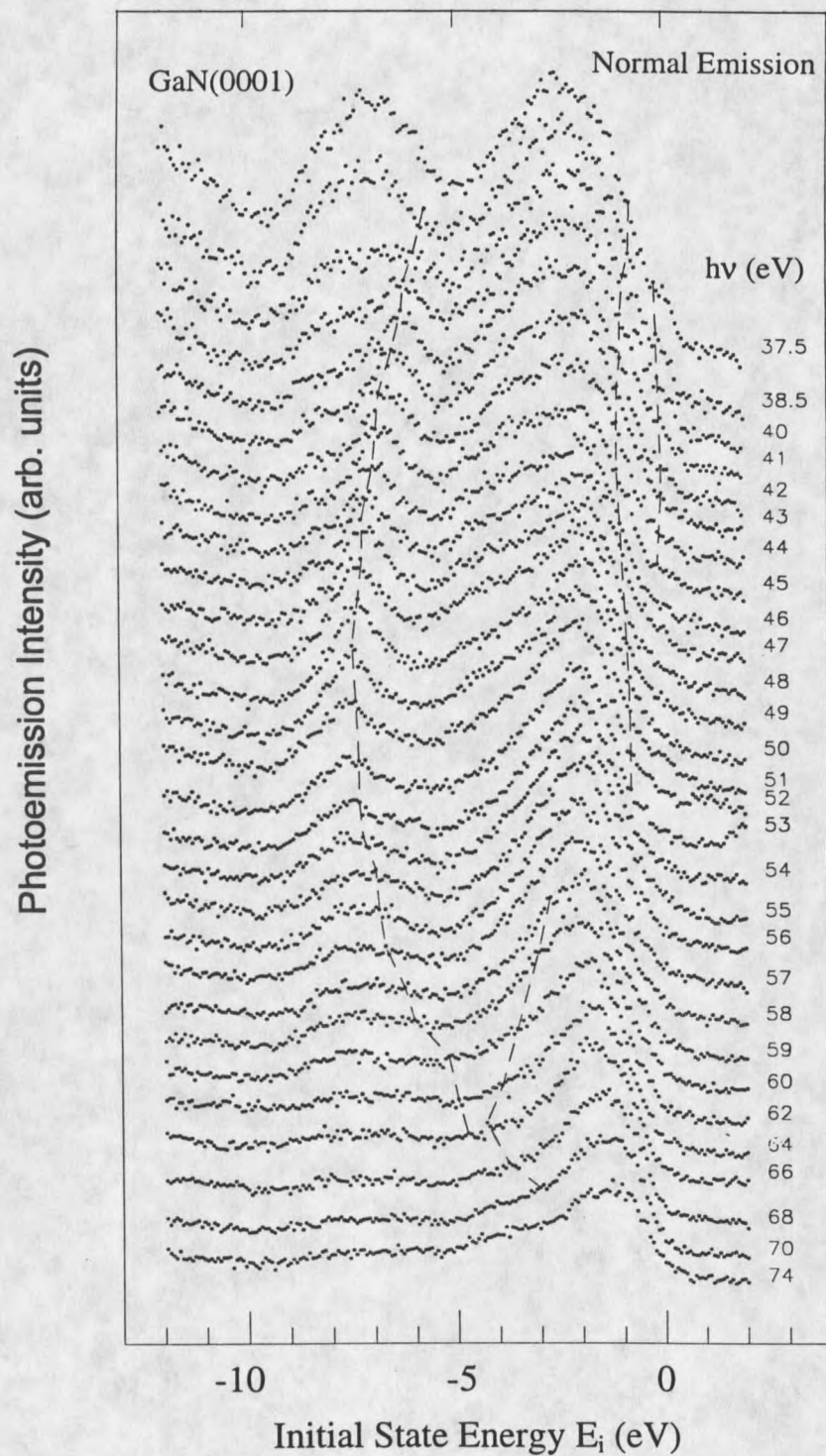


Fig. 4.6(b) Normal Emission ($\theta = 0^\circ$) taken with ERG monochromator in the photon energy range of $37.5 \leq h\nu \leq 74$ eV.

In normal emission ($\theta = 0^\circ$), the above equations become:

$$\hbar k_{\parallel} = 0 \quad (4-2a)$$

$$\hbar k_{\perp} = [2m(E_i + h\nu - E_0)]^{1/2} \quad (4-2b)$$

From equations (4-1) and (4-2), it is obvious that in the free-electron final state approximation model, there is only one adjustable parameter E_0 , where E_0 is the energy difference between the bottom of the free-electron parabola and VBM. This parameter can be determined experimentally by probing more than one Brillouin-zone in k space using the large continuous range of photon sources available, as previously explained by Horn's group.⁸⁰ This is because the various turning points of the stacked EDC's in Fig. 4.6(a) and 4.6(b) correspond to the Brillouin zone center and Brillouin zone boundaries. Thus, from the dispersion turning point in normal photoemission, we obtain $E_0 = -6.9$ eV experimentally. All of the valence band mappings along the $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Lambda K$ symmetry lines are then obtained by using the same E_0 value and k space dimensions derived from the above lattice constants. In the following discussions, we will concentrate only on the change of peak positions with photon energy. We will also ignore the spin-orbit splitting effects. For GaN, the small atomic number of nitrogen gives weaker spin-orbit interactions.⁸¹ Therefore, the spin-orbit splitting of the band structure is beyond the energy resolution of typical angle-resolved photoemission spectra.

From Figures 4.6(a) and 4.6(b), it can be seen that the upper valence band peak positions disperse clearly with the photon energy, as expected by the direct transition model. Also the intensity changes with photon energy, indicating that the cross-section

ratio ($\sigma(s)/\sigma(p)$) varies with photon energy. Nevertheless, the N 2s emission shows only a small dispersion with photon energy, which is much less than the dispersions predicted by the calculated bands.⁸²

A simple calculation using the Brillouin zone dimensions given before, along the $\Gamma\Delta A$ symmetry line, tells us that the Γ point can be reached at $2.4 \text{ \AA}^{-1}$ and $3.6 \text{ \AA}^{-1}$, and the A point can be reached at $3.0 \text{ \AA}^{-1}$ and $4.2 \text{ \AA}^{-1}$. The "mapped" valence band structure along $\Gamma\Delta A$ is shown in Fig. 4.7, together with the nomenclature⁸² used for the high symmetry points (Γ_3^v, A_{13}^v etc.). Using equation (4-2b), one can see that the A_{13}^v point (see Fig. 4.7) is probed with a photon energy of 33 eV ($k_{\perp}=3.04 \text{ \AA}^{-1}$) along $\Gamma\Delta A$ (see Fig. 4.6(a)). The overall mapped valence band in Fig. 4.7 agrees well with the calculated bands (dashed lines in Fig. 4.7).

Notice that the intensity ratio of the valence band feature at about -6 eV (derived from Ga 4s-N 2p) to that of upper valence band feature at about -2 eV (derived from Ga 4p- N 2p) changes with increasing of photon energy (see Fig. 4.6(b)), indicating that the matrix elements did play a role, as observed earlier by R. W. Hunt⁸³ et. al.

The peak at initial energy E_i about -6.8 eV is almost non-dispersive in the photon energy range of 22 to 30 eV (Fig. 4.6(a)). This non-dispersive peak has also been observed in cubic GaN by S. A. Ding⁸⁴ et. al. and could be due to indirect emission from the critical point Γ_3^v . A stationary peak at this energy is generally found in photoemission spectra from III-V semiconductors.⁸³⁻⁸⁴

Notice also in Fig. 4.6(a), there is a feature (shoulder) located just below the VBM which is non-dispersive for $23 \leq h\nu \leq 35 \text{ eV}$ and falls in the gap of the projected

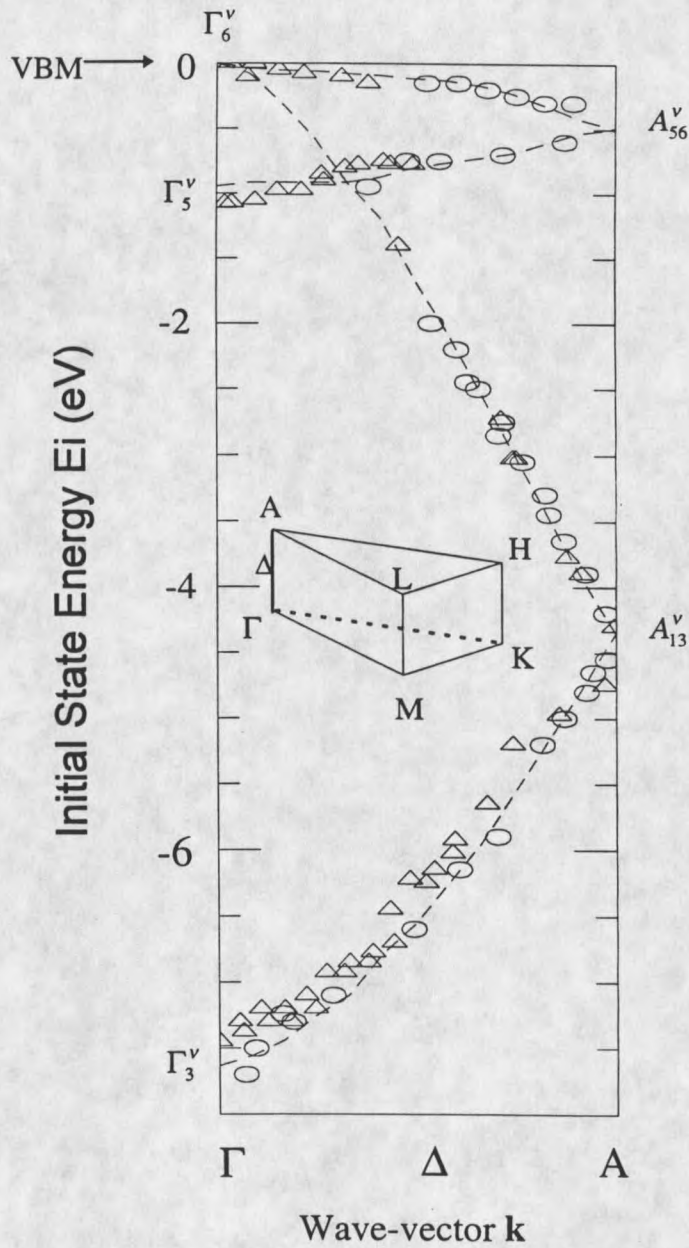


Fig. 4.7 Valence band of wurtzite GaN along $\Gamma\Delta A$. The dashed line is from the calculated band. Data in circles are obtained from Figure 4-6(a), and Data in triangles are obtained from Figure 4-6(b).

bulk bands at the Γ point. The non-dispersive behavior of this feature in normal emission resembles the characteristic expected for a surface state, which we will discuss more in later sections.

The larger initial energy peaks in Fig. 4.6 (a) are due to conduction band final states. This is shown more obviously by plotting the EDC's on the same kinetic energy scale $14 \leq h\nu \leq 32$ eV, as shown in Fig. 4.8. The inelastically scattered electrons give rise to the two peaks in Fig. 4.8 with fixed kinetic energies. These inelastically scattered electrons carry information about the conduction band final states.⁴⁹⁻⁵¹ The maxima in the conduction band DOS (density of states) could arise from contributions from more than one critical point.⁸⁵ The calculated conduction band DOS maxima appear at energies 5.9, 7.6, 8.6 eV according to Olsen,⁸⁵ and 6.1, 7.8 and 8.9 eV according to Bloom et al.⁸⁶ More recent calculations show that the conduction band DOS maxima appear at energies of about 6.1, 8.0, 10.0 eV, with the total DOS at these energies coming mainly from the partial DOS of Ga rather than from the partial DOS of the N sublattice.⁸⁷ From Fig. 4.8, values of 7.5 and 9.7 eV (relative to VBM) are obtained, which is close to the above theoretical DOS maxima values.

The critical points obtained from Fig. 4.6(b) are Γ_3^v and A_{13}^v (Fig. 4.7) as probed by photon energies of 51 eV ($k_{\perp} = 3.63 \text{ \AA}^{-1}$) and 66 eV ($k_{\perp} = 4.24 \text{ \AA}^{-1}$) along $\Gamma\Delta A$, respectively.

For the two deeper valence bands due to N 2s (initial energy around -15 eV), the photoemission intensity depends strongly on the photon energy used and is sample dependent. It can be readily seen from Fig. 4.9 that only in the photon energy range from

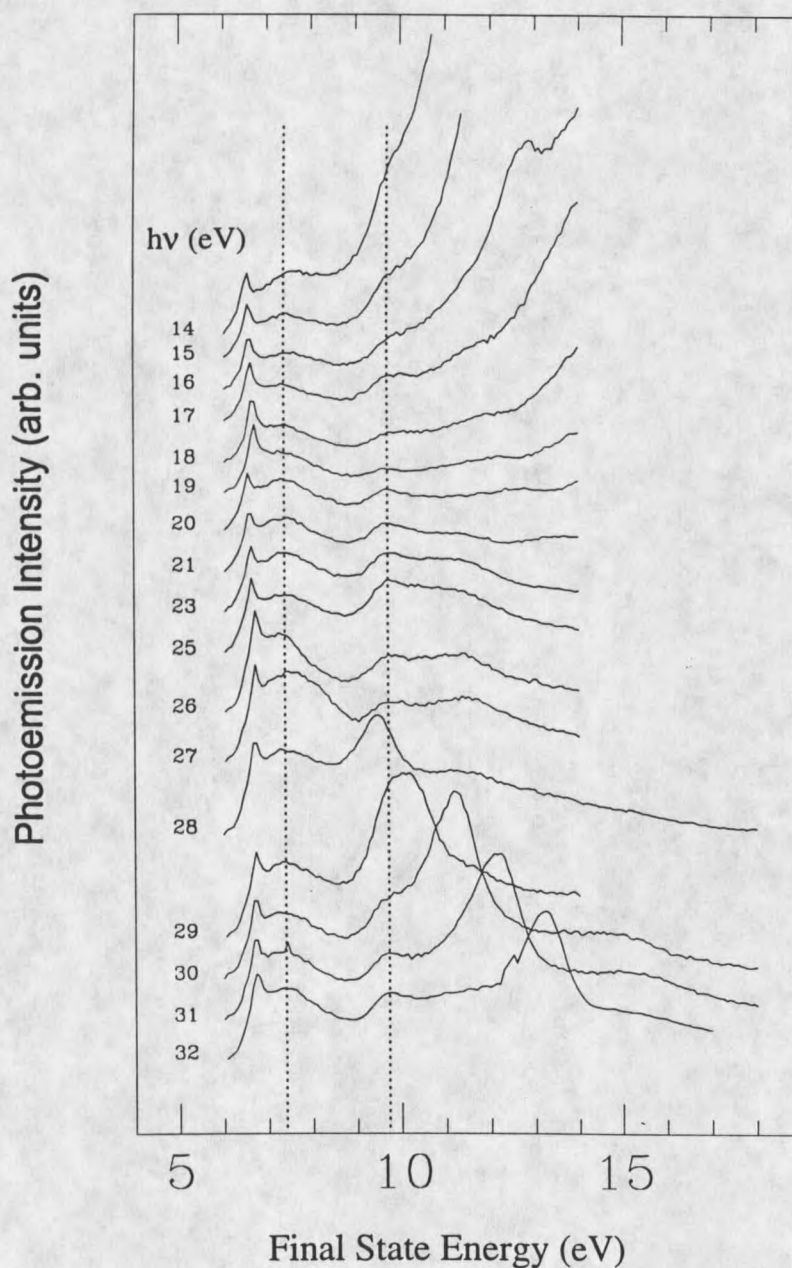


Fig. 4.8 Conduction band final states are shown by plotting the EDC's on the same kinetic energy scale with $14 \leq h\nu \leq 32$ eV. The inelastically scattered electrons, which carry the information on the conduction band final states, give rise to the two aligned peaks shown with the dashed lines. The two final state energies relative to VBM are 7.5 and 9.7 eV, which are close to the theoretical DOS.

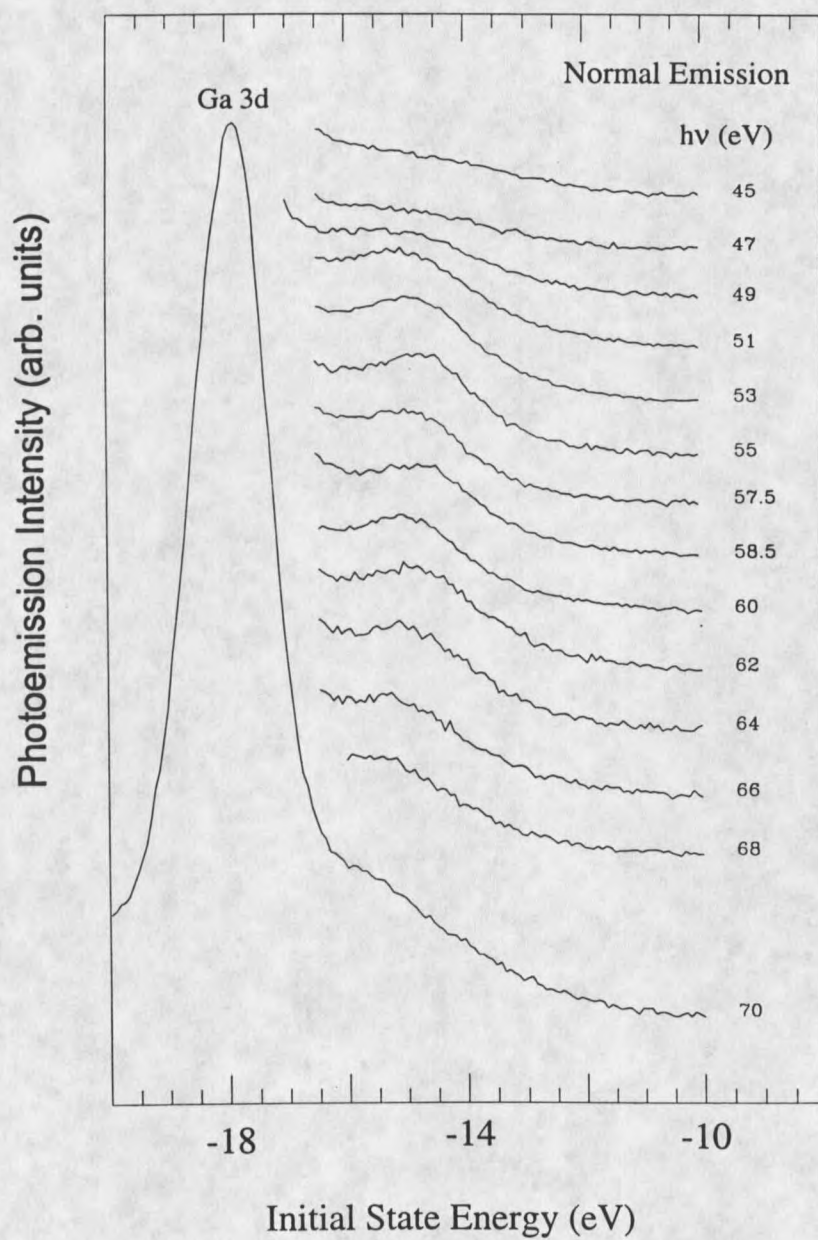


Fig. 4.9 N 2s emission as a function of photon energy $h\nu$ at normal emission. The initial energy is referenced to VBM.

49 to 68 eV, is the N 2s photoemission relatively strong. Also it disperses very little with changing photon energy. Notice that the calculated DOS of the N 2s emission is at about -13 eV below the VBM by Ming-Zhu Huang and W. Y. Ching,⁸⁸ which is not in agreement with the experimental value of -14.9 eV (see Fig. 4.4). Lambrecst and Segall²⁰ employed a so-called difference of self-consistent-fields (Δ SCF) band structure calculation, in which the binding energy is calculated as a total-energy difference including solid state screening effects by means of the excited-atom model. This excited-atom Δ SCF model gives the Ga 3d excitation energy at -17.9 eV, which is well below the N 2s band and agrees well with our experimental value of the Ga 3d emission (-17.9 eV, see Fig. 4.4).

The N 2s emission located at about 3 eV above the Ga 3d emission (Fig. 4.4) indicates that the hybridization of the N 2s and Ga 3d states is not as strong as predicted by the plane-wave pseudopotential (PWPP) method, which includes Ga 3d electrons as valence electrons and has shown N 2s bands both below and above the Ga 3d band.¹⁴

Off-Normal Emission

In off-normal emission, both the photon energy and the polar angle are changed so that the perpendicular wave-vector $k_{\perp}$ is kept fixed (see equation (4-1b)) at the Brillouin-zone center (reduced-zone scheme, $k_{\perp} \approx 3.6 \text{ \AA}^{-1}$). The probed wave-vector $\mathbf{k}$ is then determined only by $k_{\parallel}$ (equation (4-1a)). By biasing the sample negatively (usually -3V), the photo-threshold Φ_{th} is measured from the difference of the photon energy and the

width of the biased EDC curve (width from VBM to the vacuum level). In this way Φ_{th} is found to be 6 Volts.

Along the $\Gamma\Sigma M$ symmetry line, $k_{||}$ probes from the Γ point starting with $k_{||}=0$ ($\theta = 0^\circ$), to the M point with $k_{||} = 1.137 \text{ \AA}^{-1}$, and again proceeds to the Γ point with $k_{||} = 2.27 \text{ \AA}^{-1}$ and so on. $k_{\perp}$ is kept at the Γ point of about $3.6 \text{ \AA}^{-1}$, as shown in Fig. 4.10. Fig. 4.11 shows the off-normal emission data along $\Gamma\Sigma M$, starting from $\theta = 0^\circ$ at $h\nu = 49 \text{ eV}$ to $\theta = 36^\circ$ at $h\nu = 68.5 \text{ eV}$. Similarly, along the $\Gamma\Lambda K$ symmetry line, $k_{||}$ probes from the Γ point with $k_{||} = 0$ ($\theta = 0^\circ$), to the K point with $k_{||} = 1.313 \text{ \AA}^{-1}$, then to the M point with $k_{||} = 1.88 \text{ \AA}^{-1}$, and then to the K point again with $k_{||} = 2.45 \text{ \AA}^{-1}$, then again to the Γ point with $k_{||} = 3.76 \text{ \AA}^{-1}$ and so on (Fig. 4.10). $k_{\perp}$ is kept at the Γ point of about $3.6 \text{ \AA}^{-1}$. Fig. 4.12 shows the off-normal emission along $\Gamma\Lambda K$, starting from $\theta = 0^\circ$, at $h\nu = 49 \text{ eV}$, to $\theta = 36^\circ$ at $h\nu = 68.5 \text{ eV}$. The initial state energy E_i versus photon energy is called a structural plot.⁷⁸ Fig. 4.13(a) and 4.13(b) show the structural plots along $\Gamma\Sigma M$ and $\Gamma\Lambda K$.

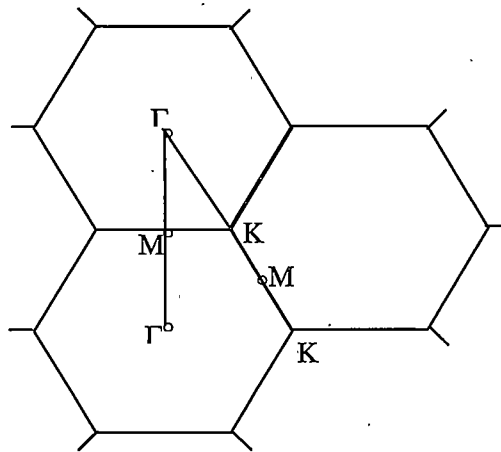


Fig. 4.10 Two dimensional Brillouin-zone. The high symmetry lines along $\Gamma\Sigma M$ (Γ -M- Γ -M...) and $\Gamma\Lambda K$ (Γ -K-M-K- Γ ...) are shown.

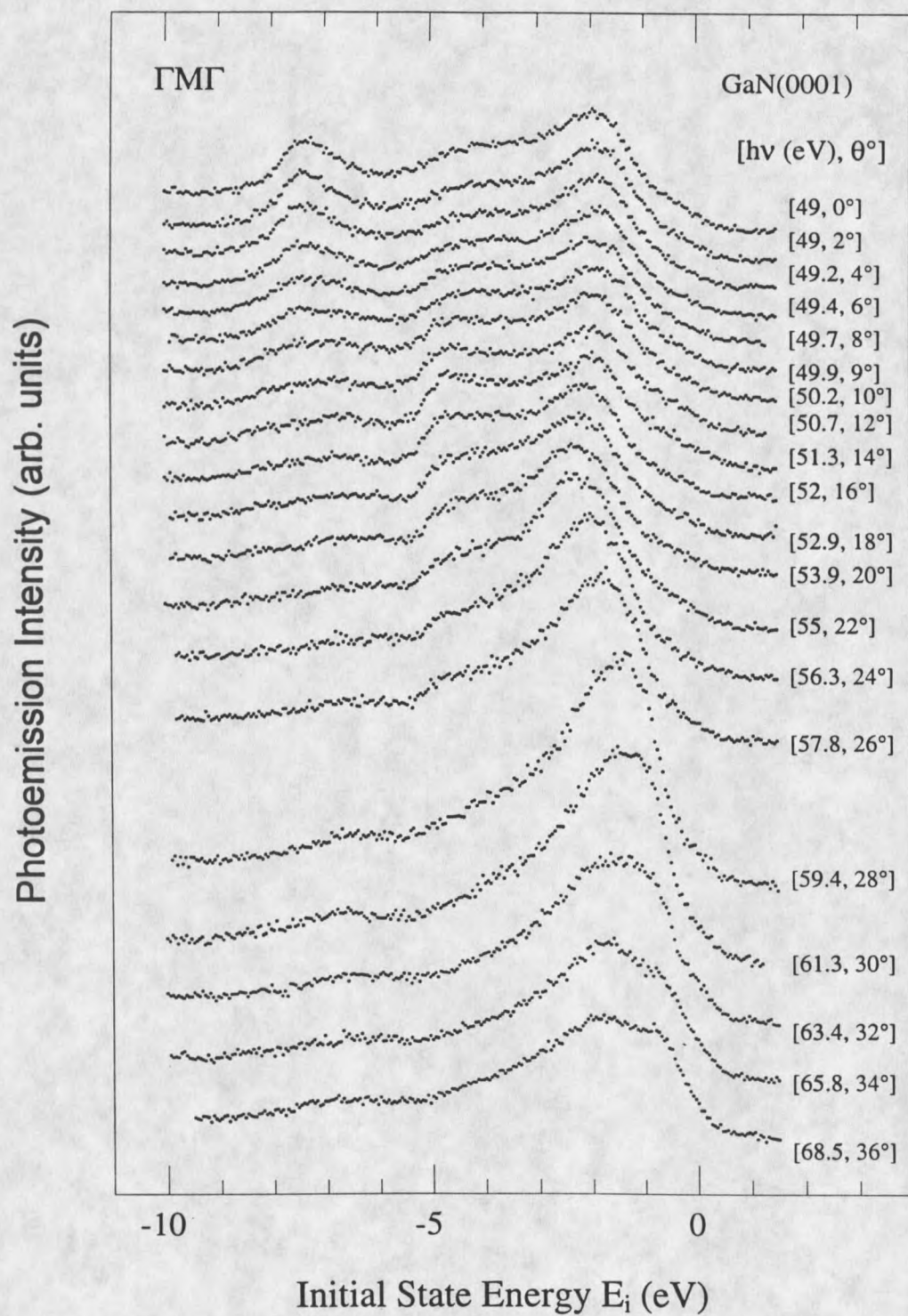


Fig. 4.11 Off-normal emission along $\Gamma\Sigma M$, starting from $\theta = 0^\circ$, at $h\nu = 49$ eV, to $\theta = 36^\circ$ at $h\nu = 68.5$ eV.

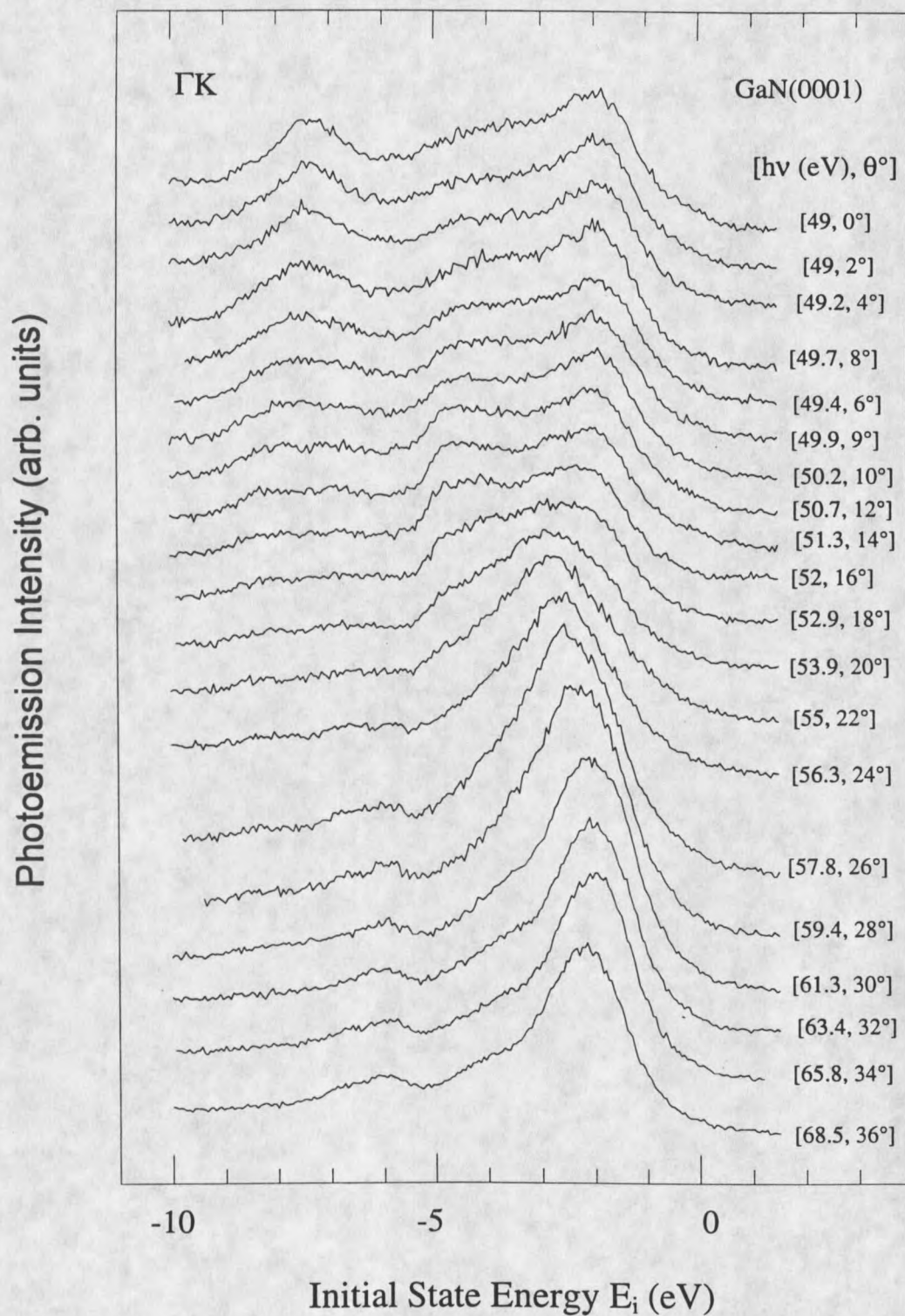


Fig. 4.12 Off-normal emission along ΓK , starting from $\theta = 0^\circ$, at $h\nu = 49$ eV, to $\theta = 36^\circ$ at $h\nu = 68.5$ eV.

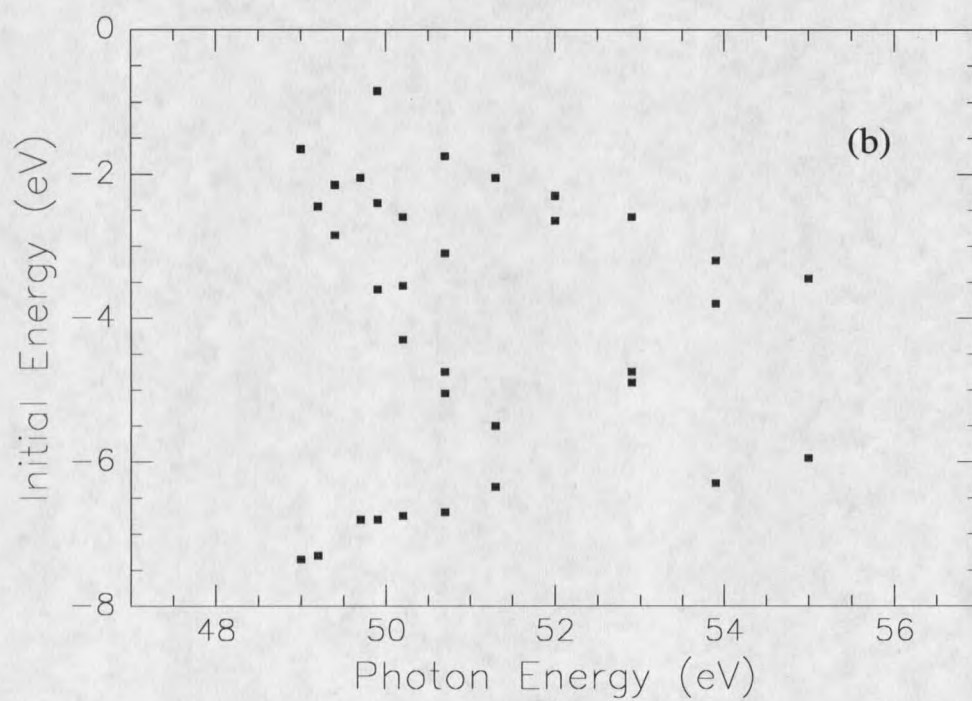
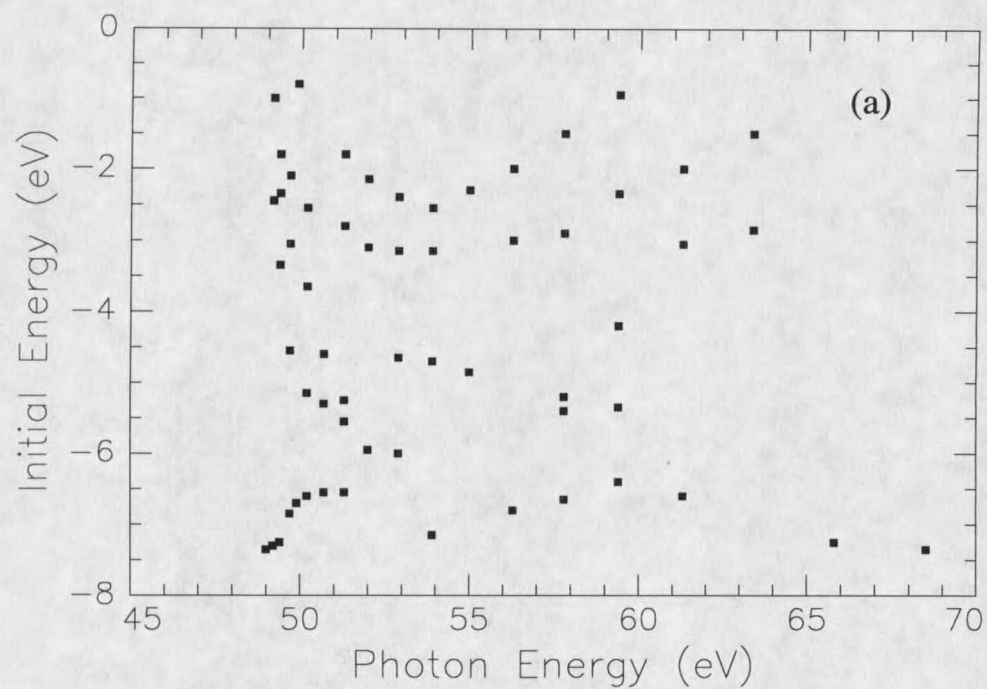


Fig. 4.13 Structural plot (a) along $\Gamma\Sigma M$ and (b) along $\Gamma\Lambda K$.

The “mapped” valence bands along the $\Gamma\Sigma$ M and $\Gamma\Lambda$ K symmetry lines are shown together in Fig. 4.14. The calculated bands are plotted as dashed lines ⁸⁶ in Fig. 4.14 and some critical points nomenclature are also shown. There is a good agreement between the off-normal emission experimental results and the calculated bands.

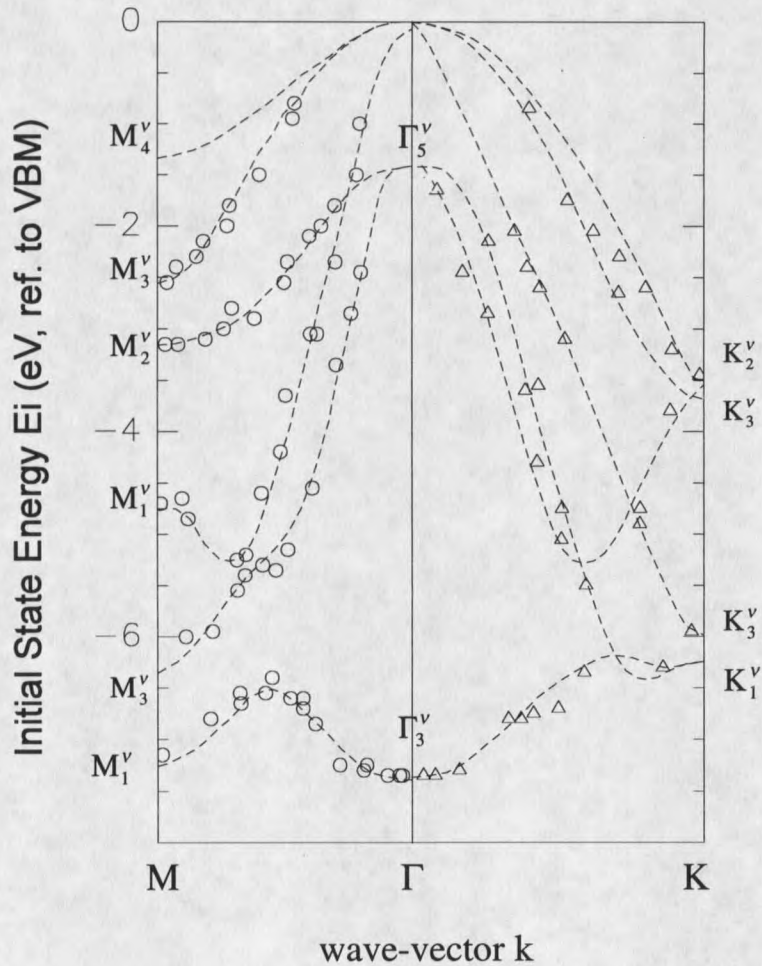


Fig. 4.14 The “mapped” valence bands along the $\Gamma\Sigma$ M and $\Gamma\Lambda$ K symmetry lines are shown together. The calculated bands are plotted as dashed lines and some critical point nomenclature is indicated.

Surface State

In order to further test the feature near the VBM (Fig. 4.6(a)), a slight contamination of bromine (15 mA sec) gas dosed from a electro-chemical BrAg cell (Br coverage well below one monolayer) is conducted on the clean surface. The feature is significantly quenched as shown in Fig. 4.15. Similar quenching of the feature upon slight evaporation of metal species (Al, Ga) is also observed. The sensitivity to the contamination test, together with the non-dispersive behavior in the normal emission, suggest it being due to an occupied surface state.

In order to investigate the dispersion of the above occupied surface state peak (shoulder) just below the VBM, as a function of the parallel component of the wave-vector, we collected EDC's with a fixed photon energy of 32 eV and changed polar angle from 0° to 70° along both ΓM (AL) and ΓK (AH), as shown in Fig. 4.16 and 4.17. It can be seen from Fig. 4.16 and 4.17 that the peak position just below the VBM changes by less than 0.4 eV with changing polar angles.

Also notice that the peak position at initial energy -6.8 eV stays about the same with changing polar angles, in Fig. 4.15 and 4.16 ($h\nu = 32$ eV), similar to its behavior with changing photon energy as seen in Fig. 4.6(a) (Seya normal emission). This seems to further suggest that the peak at about -6.8 eV is due to indirect emission from the critical point of the conduction band.

The apparent surface state feature near the VBM seems to be sensitive to the cleaning procedure and the particular sample used. For a surface annealed under gallium

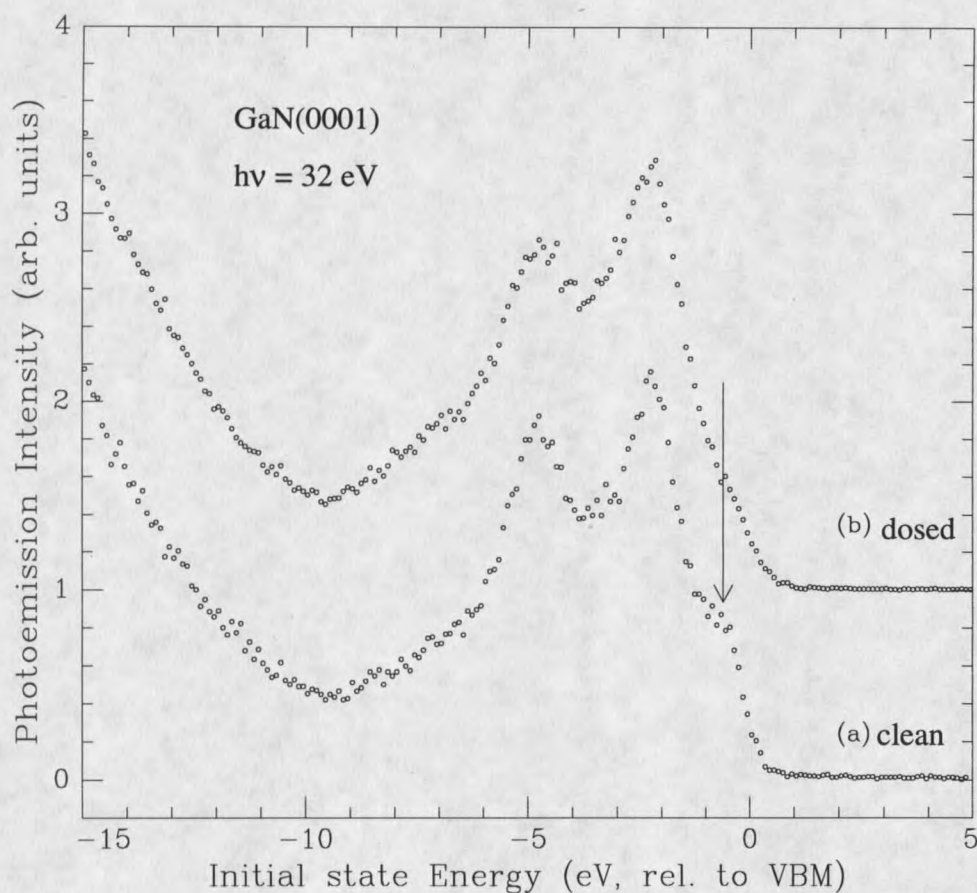


Fig. 4.15 EDC's taken at a photon energy of 32 eV on a (a) clean GaN surface and (b) a bromine dosed (15 mA sec) GaN surface. The shoulder below VBM is significantly quenched in (b).

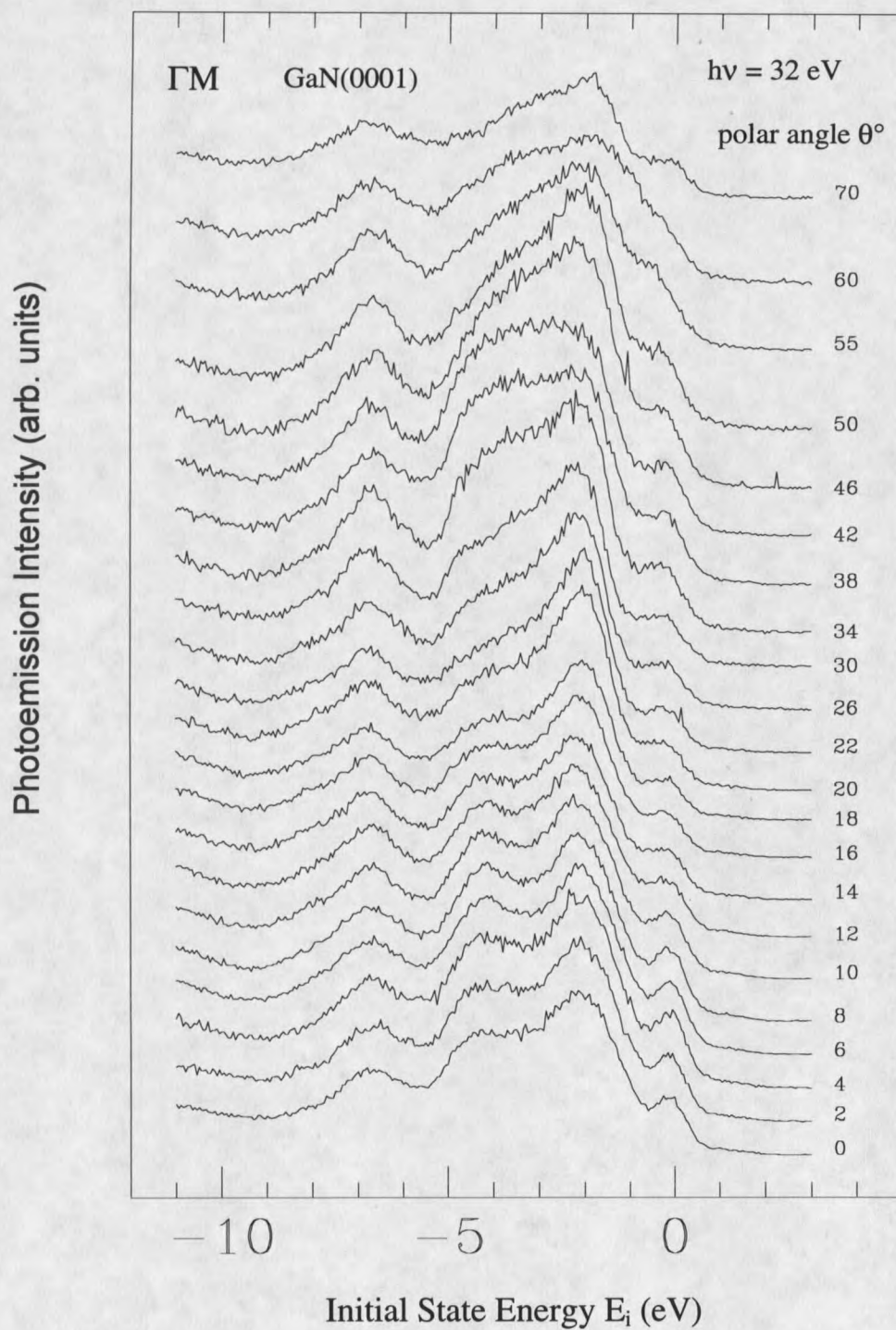


Fig. 4.16 EDC's taken with the polar angle changing from 0° to 70° along ΓM with a fixed photon energy of 32 eV.

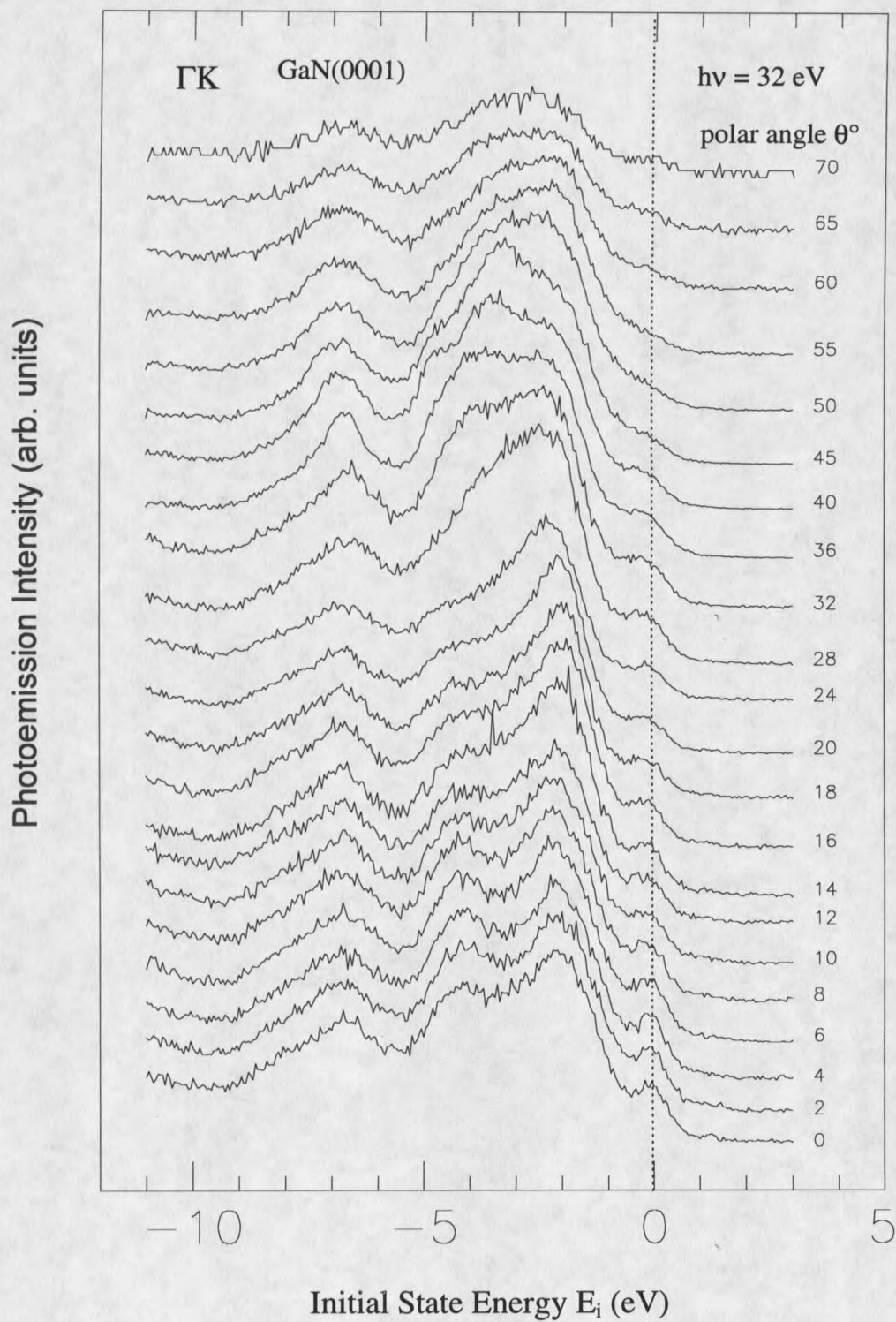


Fig. 4.17 EDC's taken with the polar angle changing from 0° to 70° along ΓK with a fixed photon energy of 32 eV.

flux, the feature is closer to the VBM (located at about -0.1 eV), while for a surface annealed without gallium flux, or a surface first covered with a thick layer of Ga and then annealed without Ga flux, the feature is further below the VBM at about -0.5 eV. Similar spectra to Figures 4.15 and 4.16 have been collected for a sample cleaned by annealing without Ga flux. The overall valence band features are similar to those obtained from the sample annealed under Ga flux.

Summary

Angle-resolved photoemission, using synchrotron-radiation, has been employed to obtain the valence band dispersions $E(\mathbf{k})$ along the three major symmetry lines $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Delta K$ of the Brillouin-zone for the wurtzite GaN structure. The results can be explained by the direct transition model, as evidenced by the dispersion of the valence band features with changing photon energy and polar angle. Valence band dispersions along the $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Delta K$ symmetry lines of the Brillouin-zone are obtained by the nearly free-electron final states approximation. The experimental results agree well with the calculated bands. Table 4.1 gives the critical point energies at Γ , K, M, A, obtained from normal and off-normal photoemission and comparisons with various calculated values. The nomenclature for these high symmetry points can be refereed to Fig. 4.7 and Fig. 4.14.

A relatively broad N 2s peak is found to have strongest photoemission intensity in the photon energy range $50 \leq h\nu \leq 65$ eV. It is found disperse very little with changing

Table 4.1 Wurtzite GaN valence band high symmetry point energies (in eV) obtained from this work, and the comparison to the various calculated values. The VBM is the energy reference level. The upper and total valence band bandwidths are $|\Gamma_3^v|$ and $|\Gamma_1^v|$, respectively.

	<i>LDA</i> ^a	<i>GW</i> ^b	<i>OLCAO</i> ^b	<i>LCAO</i> ^c	<i>This work</i>
Γ_3^v	-13.8	-15.7		-15.4	-14.9
Γ_3^v	-7.4	-8.0	-7.26	-6.78	-7.5
Γ_5^v	-1.1	-1.2		-0.96	-1.1
K_3^v	-5.5	-6.1			-6.0
K_2^v	-3.2	-3.5			-3.45
M_1^v	-6.8	-7.4			-7.15
M_3^v	-5.6	-6.1			
M_1^v	-4.4	-4.9			-4.7
M_2^v	-2.8	-3.1			-3.2
M_3^v	-2.4	-2.6			-2.55
A_{13}^v	-4.1	-4.6		-3.86	-4.35
upper- valence bandwidth	7.4	8.0	7.26	6.78	7.5
total valence bandwidth	16.3	18.2	16.03	15.40	14.9

^a Angel Rubio et al., Phys Rev. B **48**(16), 11810 (1993).

^b Yong-Nian Xu and W. Y. Ching, Phys Rev. B **48**(7), 4335 (1993).

^c Ming-zhu Huang and W. Y. Ching, J. Phys. Chem. Solids, **46**(8), 977 (1985).

photon energy at normal emission and is located at about -14.9 eV referenced to the VBM, which is about 3 eV above the Ga 3d core emission (-17.9 eV). This indicates that the hybridization of the N 2s and Ga 3d states is not as strong as predicted by the PWPP method which includes the Ga 3d electrons as valence electrons in the calculations and has shown N 2s band both below and above the Ga 3d band.

The feature near the VBM does not disperse in normal emission and disperses 0.4 eV when changing the polar angle. Together with the Bromine contamination test, this feature is assigned to an occupied surface state.

CHAPTER 5

PHOTOELECTRON DIFFRACTION IMAGING OF Al/GaN(0001)

Nature of the Terminating Wurtzite GaN Surface

Similar to other conventional III-V compound semiconductors, (for example the (111)A and (111)B surfaces of GaAs corresponding to the Ga and As terminated surfaces, respectively), the polar surface of GaN grown on the (0001) basal plane of sapphire can result in one of the following surfaces. One is the so-called (0001) surface which is gallium terminated, and the other is the $(000\bar{1})$ surface which is nitrogen terminated. Occasionally both polarity surfaces can be found in a macroscopic region on a single wafer.⁸⁹ The initial nucleation stage and the pretreatment of the substrate surfaces have significant effects on the polarity of the growing film. The question of the surface polarity is in no way a trivial issue. Indeed it has been a controversial issue in recent years.

Ion Scattering Spectroscopy (ISS) Fundamentals⁹⁰

Ion Scattering Spectroscopy (ISS), also refereed to as Low-Energy Ion Scattering (LEIS), is particularly useful for first-monolayer surface analysis. Incident ions, typically with energy of 1-10 keV, are scattered from the surface atoms and are detected by an electrostatic analyzer, as depicted in Fig. 5.1. Only charged particles are detected, and

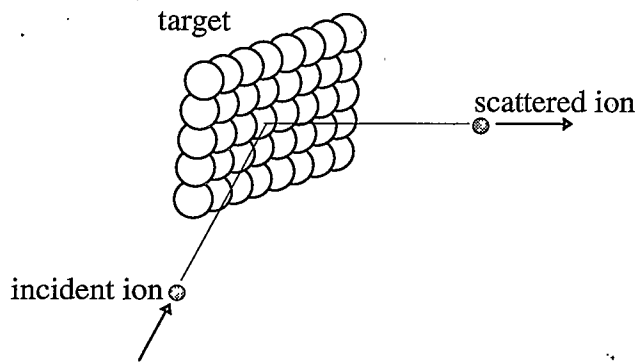


Fig. 5.1 Schematics of Ion Scattering Spectroscopy (ISS).

for particles of energy less than 1 keV, those which penetrate beyond a monolayer almost always emerge as neutral atoms. This selectivity of only charged particles greatly increases the surface sensitivity of the technique.

The kinematics of elastic collisions can be solved by applying conservation of energy and momentum. For an incident energetic particle of mass M_1 , velocity $\mathbf{v}$ and energy E_0 ($E_0 = \frac{1}{2}M_1v^2$), initially the target atom of mass M_2 is at rest. After the collision, the velocity and energy of the projectile and the target atom are $\mathbf{v}_1$, E_1 and $\mathbf{v}_2$, E_2 , respectively, as shown in Fig. 5.2. Applying conservation of energy and momentum, we get:

$$\left\{ \begin{array}{l} \frac{1}{2}M_1v^2 = \frac{1}{2}M_1v_1^2 + \frac{1}{2}M_2v_2^2 \\ M_1v = M_1v_1\cos\theta + M_2v_2\cos\varphi \\ 0 = M_1v_1\sin\theta - M_2v_2\sin\varphi \end{array} \right. \quad (5-1)$$

Eliminating ϕ and then v_2 , we get:

$$\frac{v_1}{v} = [\pm(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta] / (M_1 + M_2) \quad (5-2)$$

Letting $A = M_2/M_1$, from equation (5-2), if $M_2 < M_1$, there exists a critical angle $\theta_c = \sin^{-1}(A)$ above which only multiple scattering can occur.⁹⁰ For a single collision of the projectile into an angle ϕ , it is called the direct recoil. Therefore, the ratio of the projectile energies for $M_1 < M_2$ is:

$$\frac{E_1}{E_0} = \left\{ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{(M_1 + M_2)} \right\}^2 \quad (5-3)$$

The energy ratio E_1/E_0 is called the kinetic factor K . From the above equation, the energy after scattering is only a function of target mass M_2 , if one takes the projectile mass M_1 , scattering angle θ , and incident ion energy E_0 to be constants in an experimental setup.

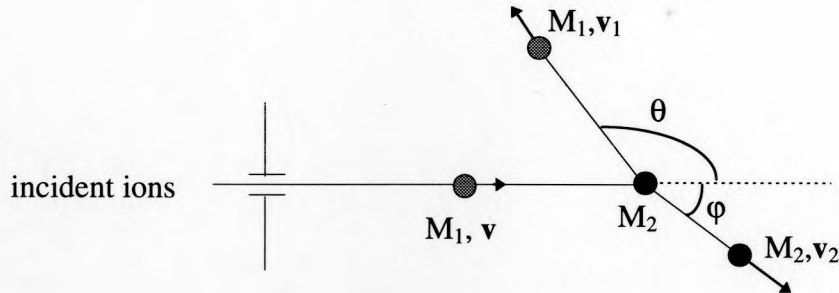


Fig. 5.2 Schematics of an elastic collision between a projectile of mass M_1 and a target of mass M_2 initially at rest.

Thus the ISS spectra consist of peaks corresponding to the atomic masses of the sample surface layer. In our case, $M_1 = 4$, $\theta = 130^\circ$, so the kinetic factors of Ga, N, O and C are 0.82796, 0.37955, 0.43117 and 0.3186, respectively. With an incident ion energy of 600 eV, the corresponding detected energies for Ga, N, O and C will be at 496.8 eV, 227.7 eV, 258.7 eV and 191.2 eV, respectively.

ISS Measurements and the Model of Al adsorption Sites

Fig. 5.3 is the experimental ISS spectrum taken from a wurtzite GaN sample. An electrostatic analyzer is used to measure the kinetic energies of ions. The dominant peak is located at 497.5 eV, which is clearly due to the surface Ga atoms. Apart from the major Ga-originated peak, there are two smaller peaks at energies about 213.5 eV and 244 eV, which are 48 and 40 times smaller than the Ga-originated peak. No carbon-induced peak is detected after appropriate annealing up to about 700°C.

There is an energy offset of about 15 eV of the two detected small peaks relative to the calculated N and O peak positions. Nevertheless, the separation between the two small peaks (30.5 eV) is close to the predicated separation value (30.8 eV) between N and O. Therefore the two small peaks are most probably due to a small amount of oxygen on the surface and the unshadowed nitrogen atoms from the bilayer (0001) face in the case of a Ga terminated surface. If no surface relaxation occurs, the (0001) Ga terminated face is a bilayer composed of a top Ga layer and an unshadowed N layer about 0.65 Å below the terminating Ga layer (see Fig. 5.5 later). The small separation of the (0001) bilayer of Ga and N could very possibly lead to a detectable nitrogen ISS signal.

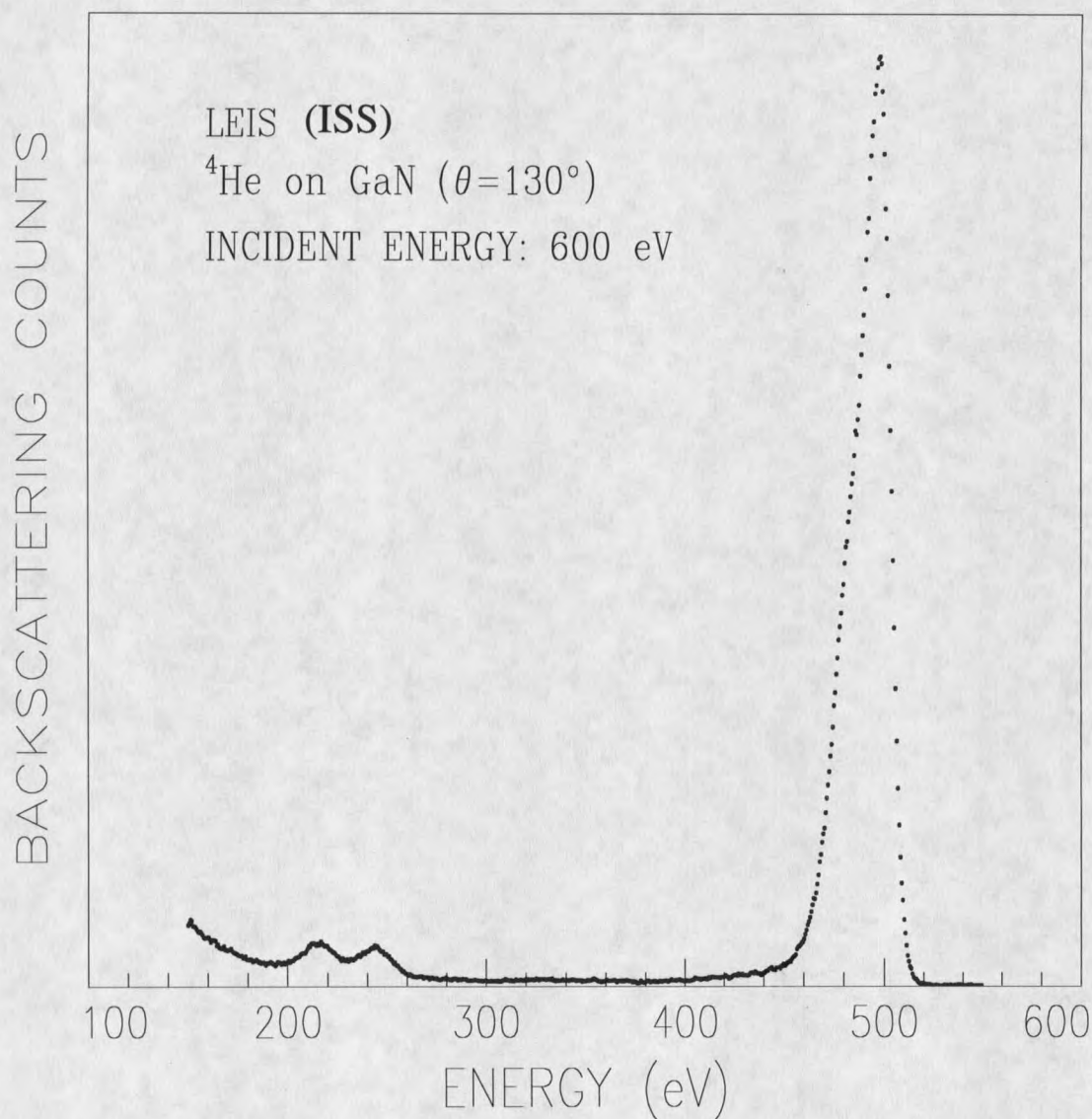


Fig. 5.3 Ion Scattering Spectroscopy (ISS) of incident ${}^4\text{He}$ on a GaN(0001) surface. The dominant peak at 497.5 eV is due to surface Ga atoms.

For the large Ga peak in the ISS data (Fig. 5.3), it seems tempting to jump to the conclusions that the surface is the Ga terminated (0001) face. However, the GaN basal surfaces are more complicated, as published very recently by J. E. Northrup's group.⁹¹

On a nitrogen terminated ($000\bar{1}$) surface, J. E. Northrup's group recently discovered that the 1×1 reconstruction consists of a monolayer of Ga atoms located in atop sites (forming a Ga adlayer) above the N terminated N atoms, as shown in Fig. 5.4. Thus for a ($000\bar{1}$) N terminated surface, it would be unlikely to detect any ISS signal from the substrate N atoms, since in this case the nearest nitrogen atoms relative to the surface are about 2 Å below the Ga adlayer. Furthermore, they are shadowed by the overlaying Ga adlayer atoms at the atop sites. Therefore the ISS data seem to suggest that the surface is most likely the Ga terminated (0001) surface.

However the determination of the polarity of the wurtzite GaN basal surface could be a complex issue. There has been a report using Convergent Beam Electron diffraction (CBED) to determine the surface polarity of wurtzite GaN films.⁹²

A recent study by M. Seelmann-Eggebert et al.⁸⁹ used an etching technique and a hemispherical scanned x-ray photoelectron diffraction (HSXPD) method to determine the surface polarity. They found that the nitrogen terminated epilayer has a generally rough surface morphology, as revealed by AFM (atomic force microscopy) with a RMS roughness of about 40 nm. On the other hand, the Ga-terminated (0001) GaN films are usually much smoother. Etching the polar surface with solutions of KOH or NaOH will polish the rough ($000\bar{1}$) nitrogen polarity surface to a much smoother one, with the RMS roughness decreasing from 40 nm to 0.4 nm as verified by the AFM measurements. On

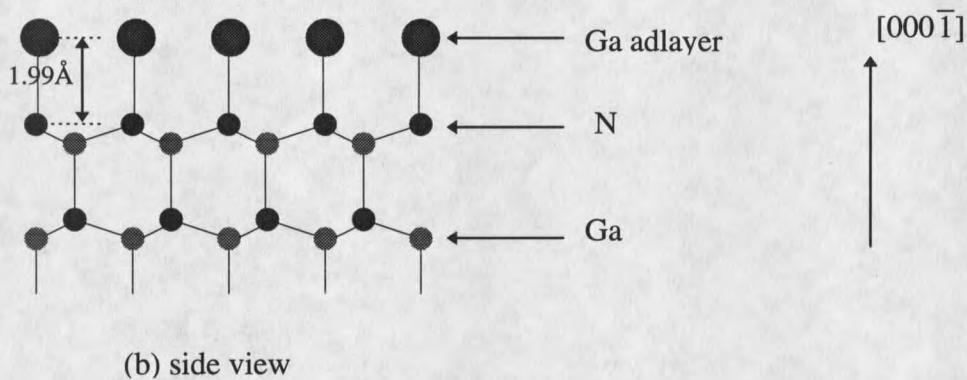
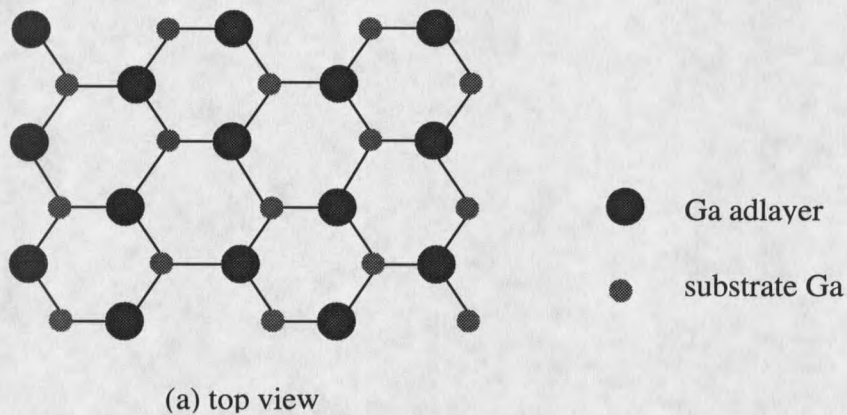


Fig. 5.4 Schematic 1×1 reconstruction of GaN(000 $\bar{1}$) Ga adlayer (a) top view and (b) side view.⁹⁰

the contrary, the Ga polarity (0001) surface is resistant to the etching process. Further experiments will be needed to unambiguously determine the surface polarity of the wurtzite GaN film, which unfortunately is not available at this stage.

As will be studied later by photoelectron diffraction imaging (PDI), a half monolayer of Al in situ deposited onto the wurtzite GaN basal surface will give signals diffracted by the substrate Ga and N scatterers detected from the Al 2p core level

emission. By a Fourier-like transformation over wave-number k and spherical mesh directions (θ, ϕ) , one can get a real space three dimensional image of the atomic arrangements surround the Al emitter.

Fig. 5.5 shows a side view of Al adsorption model on a (0001) Ga terminated surface. As revealed by the photoelectron diffraction images, the Al emitter has two inequivalent sites, one is the on top (atop) site (shown in Fig. 5.5 as Al(1)), and the other is the replacing site (shown in Fig. 5.5 as Al(2)). The strong image spot at $(0, 0, -2.05)\text{\AA}$ for RT Al/GaN and at $(0, 0, -2.15)\text{\AA}$ for annealed Al/GaN interfaces (see PDI experimental results later) both give a reasonable Al-Ga bond length of $2.05\text{-}2.15\pm0.1\text{\AA}$, which is close to the Ga-Ga bond length on a $(000\bar{1})$ N terminated surface of about $2.05\text{\AA}$.⁹⁰ Notice this bond length is also close to the adlayer Ga-N bond length of $1.99\text{\AA}$ ⁹⁰ and the bulk Ga-N bond length of $1.95\text{\AA}$.

Since both the (0001) and $(000\bar{1})$ surfaces are occupied by Ga atoms on the top surface, there is a possibility of Al adsorption on a $(000\bar{1})$ N terminated surface. Fig. 5.6 shows the schematic side view of the Al adsorption model on a $(000\bar{1})$ surface. In this case, the image at about $2\text{\AA}$ below the Al emitter could be the N atom directly below, as depicted by AL(1) in Fig. 5.6, and the image at about $3.3\text{\AA}$ below the Al emitter could be the third layer Ga atom directly below the Al(2) at a T_4 site above the Ga adlayer (Fig. 5.6). In Fig. 5.6, the Al(1) occupying the on top (atop) site is expected to have comparable scattering signals from the three fold Ga atoms which are located at about $0.65\text{\AA}$ below the terminating N atoms, as compared to signals from the N atoms directly below. This is because although the three fold Ga atoms are further away from

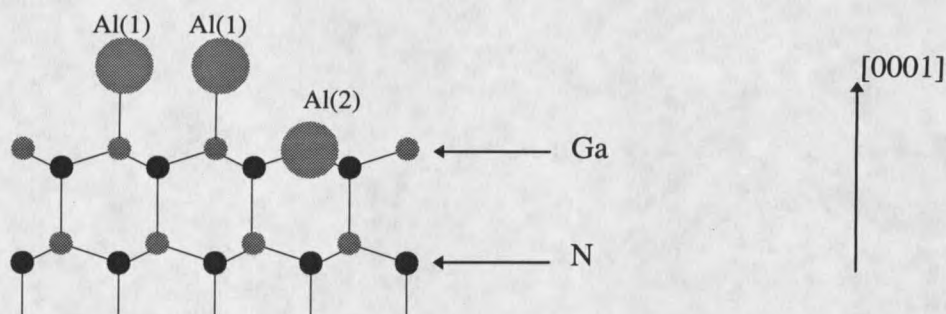


Fig. 5.5 Schematic side view of Al adsorption model on a (0001) surface.

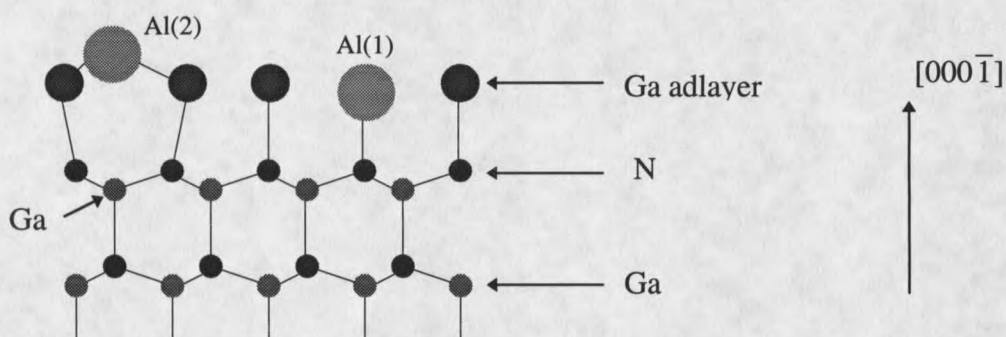


Fig. 5.6 Schematic side view of Al adsorption model on a (000 $\bar{1}$) surface.

the Al than the N atoms, the scattering amplitude of Ga could be a few times larger than that of N's. Nevertheless, no nontrivial three fold image spots at the appropriate depth are found from the photoelectron diffraction images (see Chapter 6). Therefore, the photoelectron holographic image results are best explained by a (0001) Ga-terminated surface, in agreement with our conclusion based on the ISS data.

Experiments by Photoelectron Diffraction Imaging of Al/GaN

Experimental

The experiments were performed at the University of Wisconsin-Madison Aladdin storage ring on the Iowa-Montana State ERG 2-meter monochromator beam-line. The n-type GaN(0001) sample was pressed against a silicon wafer and resistively heated through the silicon wafer. The surface cleanness was constantly checked by surface sensitive C 1s and O 1s core-level signals monitored with photon energies of 350 eV and 610 eV respectively, as well as valence band spectroscopy for the O 2p resonance. The surface thus obtained showed a good 1×1 LEED pattern and sharp valence band features, especially in the case of the surface emission (see chapter 4) just below the valence band maximum (VBM).

Al was evaporated from a three-wire twisted tungsten basket and monitored by a quartz-crystal oscillator placed next to the sample during the evaporation. The basket was half filled with 5N (99.999%) twisted Al wires to get a good Al wetting on the tungsten basket. Repetitive outgassing of the Al source was conducted until the working pressure of Al evaporation was below 6×10^{-10} Torr. The GaN sample was kept at room temperature (RT) during Al deposition. The equivalent Al coverage was about one half of a monolayer and showed a good 1×1 LEED pattern with minimal increase of background.

The images obtained from photoelectron diffraction imaging (PDI) are all relative to the Al emitter at the origin (0., 0., 0.), with the z axis along the surface normal and the xy plane chosen as in Fig. 5.7.

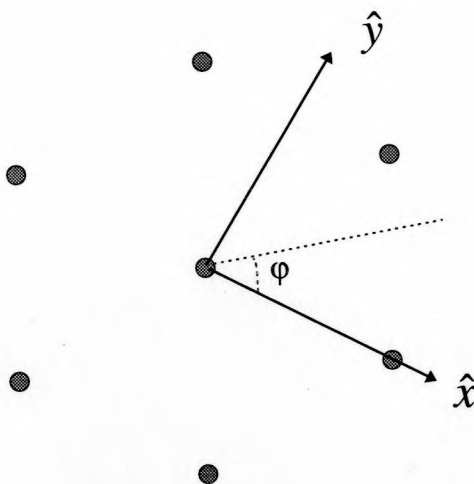


Fig. 5.7 GaN(0001)(1 $\times$ 1)-Al LEED pattern and the x, y axis chosen in the basal plane.

The sample was rotated in φ (azimuthal angle), and the analyzer in θ (polar angle), for each CIS (Constant Initial State) measurement along different outgoing photoelectron directions. Sample alignment was performed by both LEED (0, 0) beam and laser reflection. The irreducible hemispheric mesh (θ, φ) was $\theta = 0-90^\circ$ and $\varphi = 0-60^\circ$.

The (θ, φ) mesh used to collect data was $\theta = 0-75^\circ$ and $\varphi = 0-60^\circ$ for RT Al/GaN(0001) and $\theta = 0-67.5^\circ$ and $\varphi = 0-60^\circ$ for annealed Al/GaN(0001). The 60° solid angle mesh has about 1700 data points in k (momentum) space, with each data point corresponding to an energy distribution curve (EDC) spectrum. A constant polar angle increment $\Delta\theta = 7.5^\circ$ and a constant momentum increment $\Delta k = 0.15 \text{ \AA}^{-1}$ were used in all data acquisition. The increment of azimuth angle was about $\Delta\varphi = \Delta\theta/\sin(\theta)$ (rounded to the nearest integer value) in order to keep a constant solid angle increment. The photon

energy scan used in each CIS was $h\nu = 100\text{--}240$ eV, which corresponds to the k range 2.5 to $6.5 \text{ \AA}^{-1}$ for the Al 2p core-level photoemission. The Al 2p cross section behaved well (monotonically) as a function of $h\nu$, and a relatively high photon flux was available in the chosen $h\nu$ energy range. An overview EDC spectrum taken at $h\nu = 168$ eV is shown in Fig. 5.8.

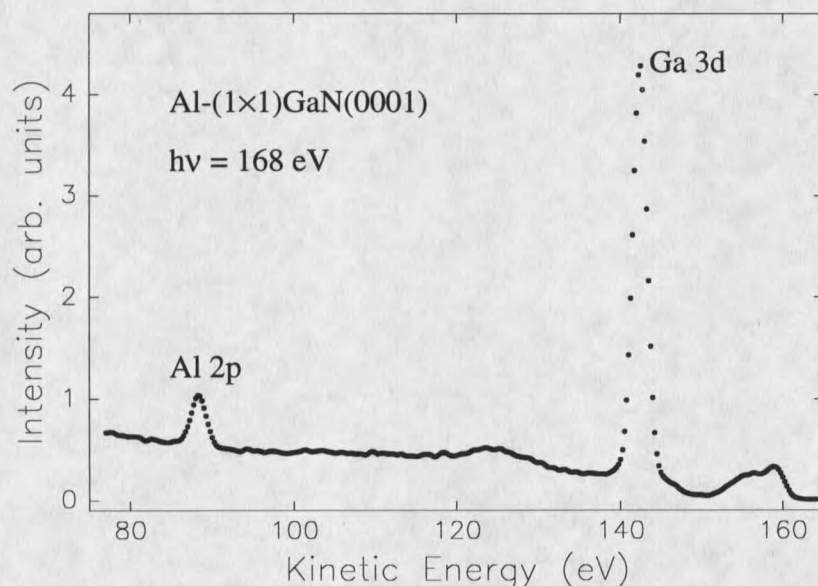


Fig. 5.8 Wide-scan energy distribution curve (EDC) for Al-(1 $\times$ 1)GaN(0001) taken at $h\nu = 168$ eV.

A typical CIS spectrum $I_k(k)$ taken at $\theta = 0^\circ$ and $\phi = 0^\circ$ for Al-(1 $\times$ 1) GaN(0001) is shown in Fig. 5.9. Each data point in $I_k(k)$ is obtained from the area of a Gaussian

fit to the Al 2p EDC spectrum, as shown in Fig. 5.9(a). A smooth background $I_0(k)$ is obtained by a spline fit (software GENPLOT) and is removed from the CIS spectrum $I_k(k)$ (Fig. 5.9(b)) to get the normalized diffraction curve $\chi(k)$ (Fig. 5.9(c)):

$$\chi(k) = I(k) / I_0(k) - 1 \quad (5-4)$$

Some representative CIS spectra, each plotted together with its smooth background $I_0(k)$ (chosen by spline fit), are shown in Fig. 5.10.

Al-(1×1)GaN(0001) at Room Temperature

Fig. 5.11 shows an xz plane cut at $y = 0.0 \text{ \AA}$ for RT Al-(1×1)GaN(0001). The cross represents the Al emitter at the origin. Two strong image spots are clearly seen from Fig. 5.11, spot 'A' located at $(0., 0., -2.05) \text{ \AA}$ with an intensity of 10.0 (arbitrary units) and spot 'D' located at $(0., 0., -3.3) \text{ \AA}$ with an intensity of 4.0. Fig. 5.12 shows the one-dimensional z-scan passing through spots 'A' and 'D'. In addition to the two main intensity peaks corresponding to spots 'A' and 'D' in the one-dimensional z-scan, two shoulders at about $z = -1.2 \text{ \AA}$ and $z = -4.2 \text{ \AA}$ respectively, can be seen from Fig. 5.12. These are the artifacts related to multiple scattering, which we will address in more detail afterwards.

Figures 5.13 and 5.14 show the one-dimensional x-, and y-scans passing through spots 'A' and 'D' and the xy plane cut at $z = -2.05 \text{ \AA}$ (spot 'A') and $z = -3.3 \text{ \AA}$ (spot 'D'), respectively. These one-dimensional scans all show a typical full width at half maximum

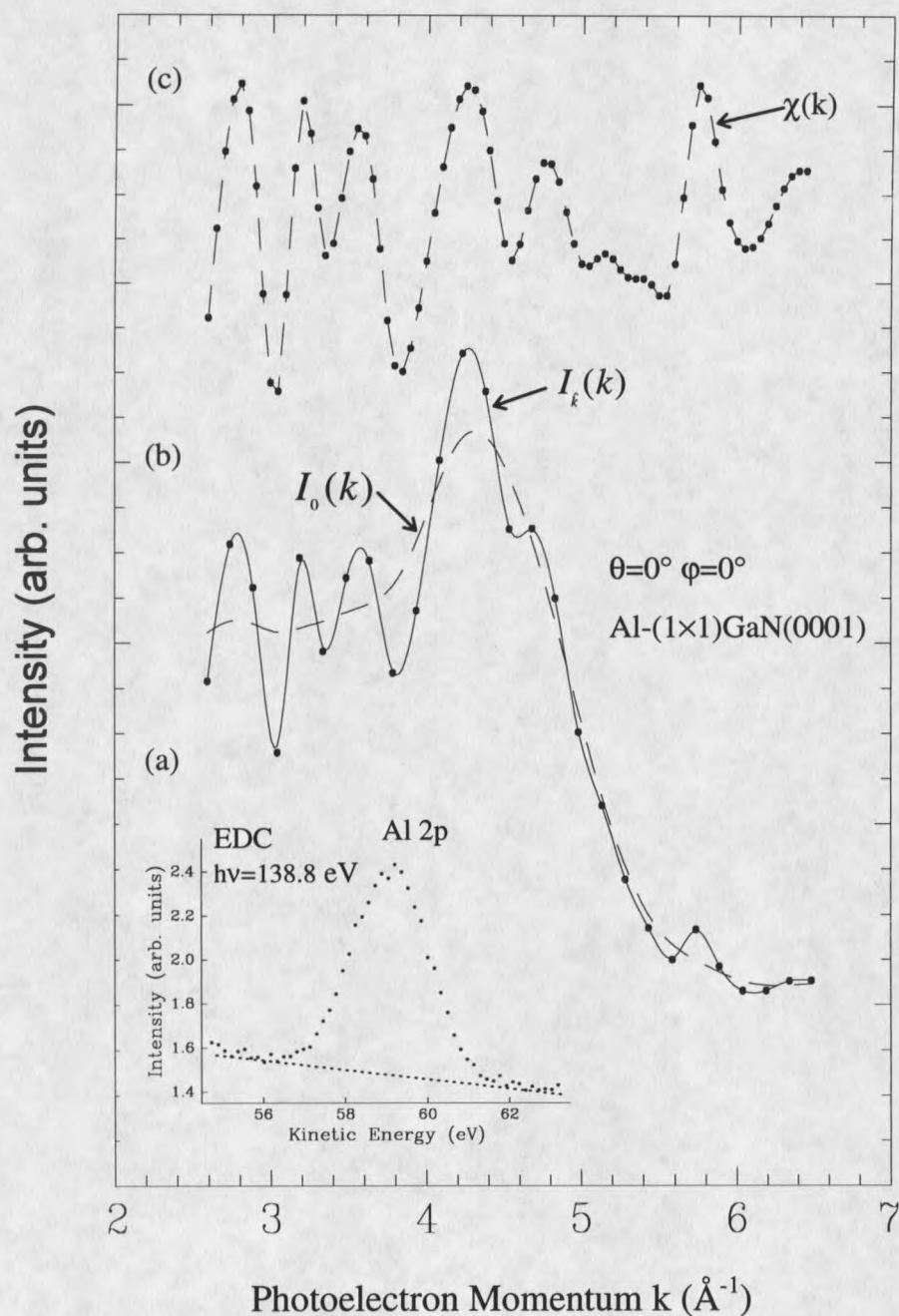


Fig. 5.9 A typical CIS spectrum $I_k(k)$ (b) and the underlying energy distribution curve (a). A smooth background $I_0(k)$ is obtained by spine fit and is removed from the CIS spectrum $I_k(k)$ to get the normalized diffraction curve $\chi(k)$ (c).

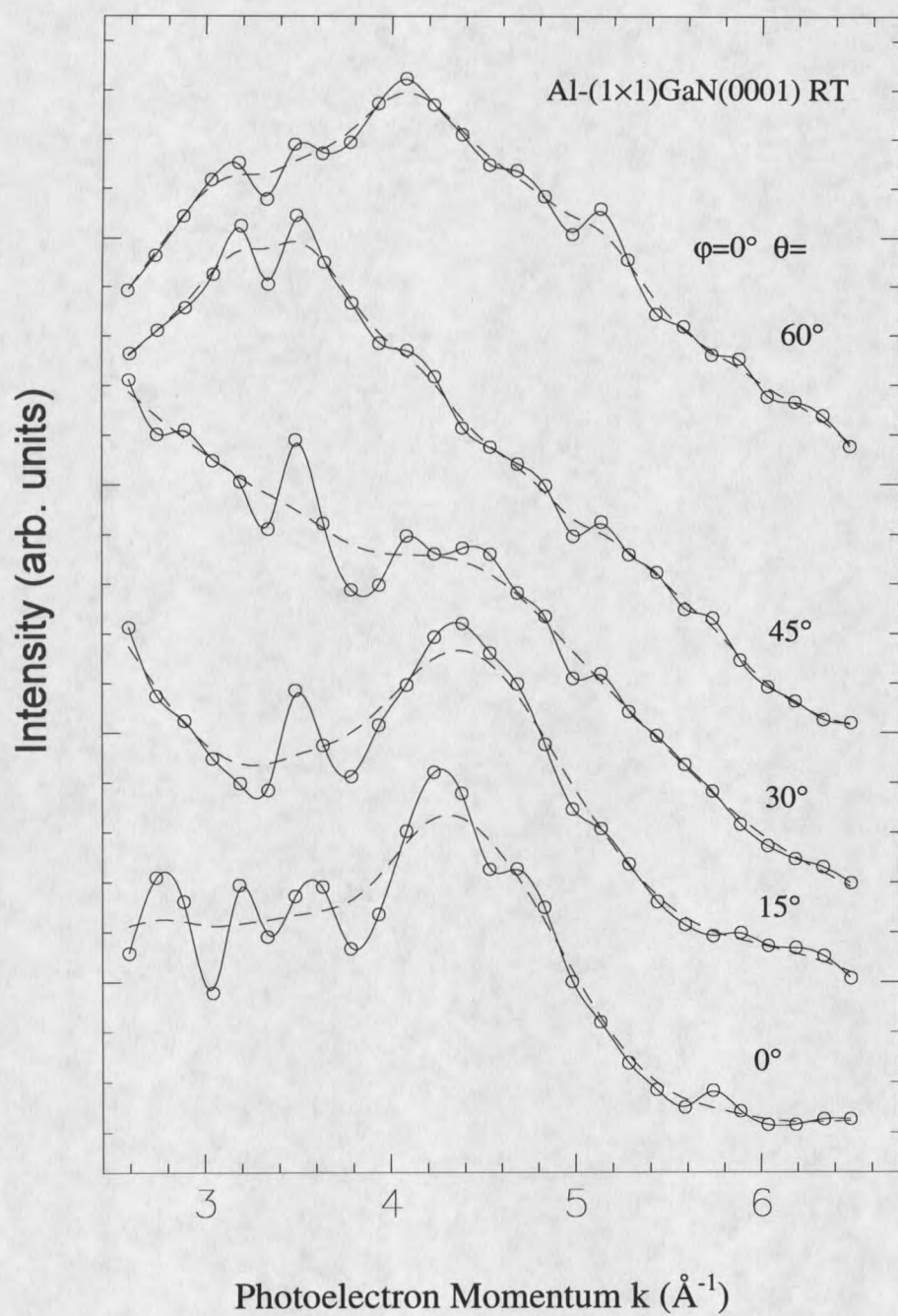


Fig. 5.10 Some representative CIS spectra at RT (solid lines), each plotted together with their smooth background $I_0(k)$ (dashed lines) obtained by a spline fit.

(FWHM) $\leq 1 \text{ \AA}$, in good agreement with theoretical predictions.⁹³

From the xz plane cut shown in Fig. 5.11, apart from the two strong image spots right below the Al emitter, no image signal is observed with intensity greater than background noise at off sample normal directions (on the side). This could be due to the following reasons. First, one of the scatterers in the substrate--nitrogen, has a small atomic number ($z = 7$) and thus could lead to a smaller degree of scattering as compared to the Ga scatterer. Second, the scattering effect is strongest in forward and backward directions. While forward scattering is not an issue here (for scatterers below the emitter), the strong signal from backward scattering by scatterers located directly below the Al emitter could be strong enough to overshadow any signals from scatterers located on the side of the emitter.

In order to utilize the data in a more appropriate way, we analyzed it using only part of the CIS spectra, with a CIS angular mesh consisting of $\theta = 52.5^\circ$ - 67.5° and $\phi = 0^\circ$ - 60° (as compared to the previous angular mesh of $\theta = 0.0^\circ$ - 67.5° and $\phi = 0^\circ$ - 60°). The image thus obtained did show a strong intensity spot off normal direction. Fig. 5.15(a) shows a xy plane cut at $z = -2.9 \text{ \AA}$. The spot 'B' located at $(1.95, 0., -2.9) \text{ \AA}$ has an image intensity of 6.03. Fig. 5.15(b)-(d) shows the one-dimensional x-, y- and z-scan passing through spot 'B'. The elongated image is due to the relatively smaller number of CIS's taken into account in the transformation.

Together with the (1×1) LEED pattern of Al/GaN(0001), we postulate the following Al adsorption site model. There are two in-equivalent sites, one is directly above the surface Ga atom, "the on-top site", as revealed by the image at $(0., 0., -2.05) \text{ \AA}$

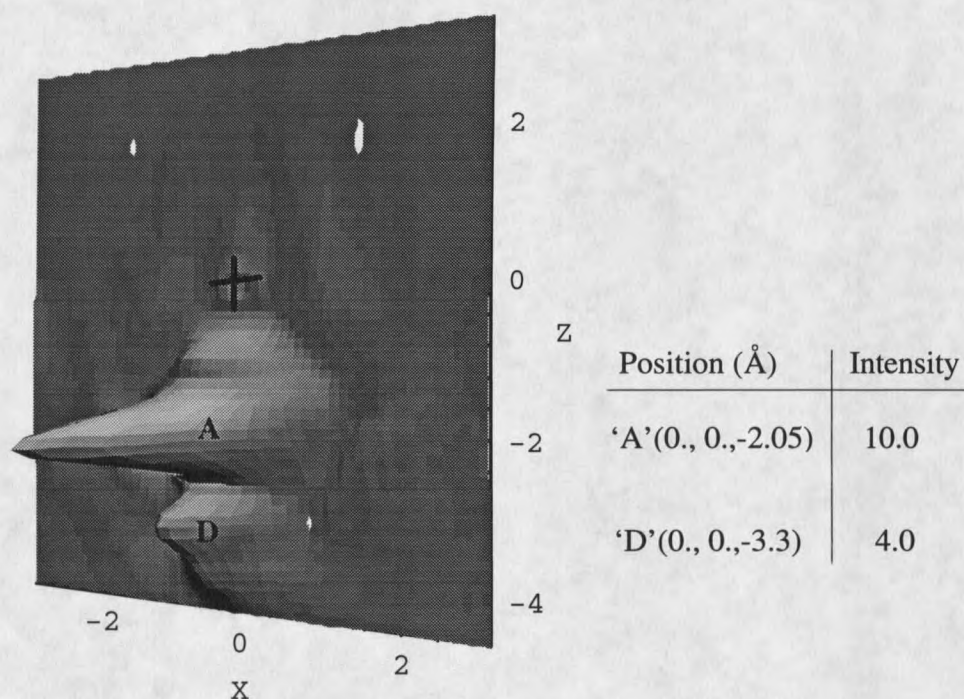


Fig. 5.11 xz plane cut at $y = 0.0\text{\AA}$ for RT Al-(1 $\times$ 1)/GaN(0001). The cross represents the Al emitter at the origin.

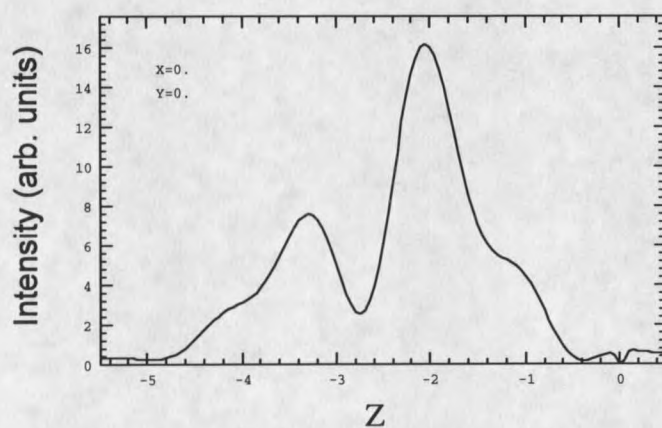


Fig. 5.12 One-dimensional scan along z axis passing through spot 'A' and 'D' at RT.

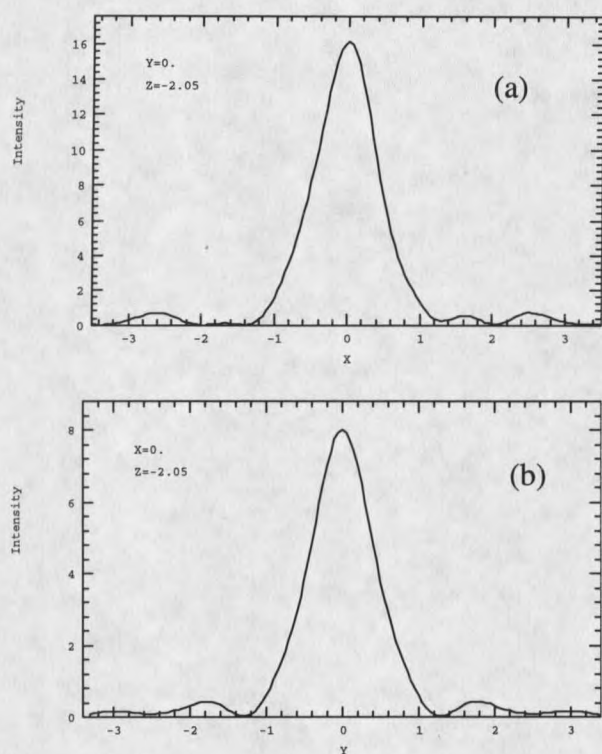
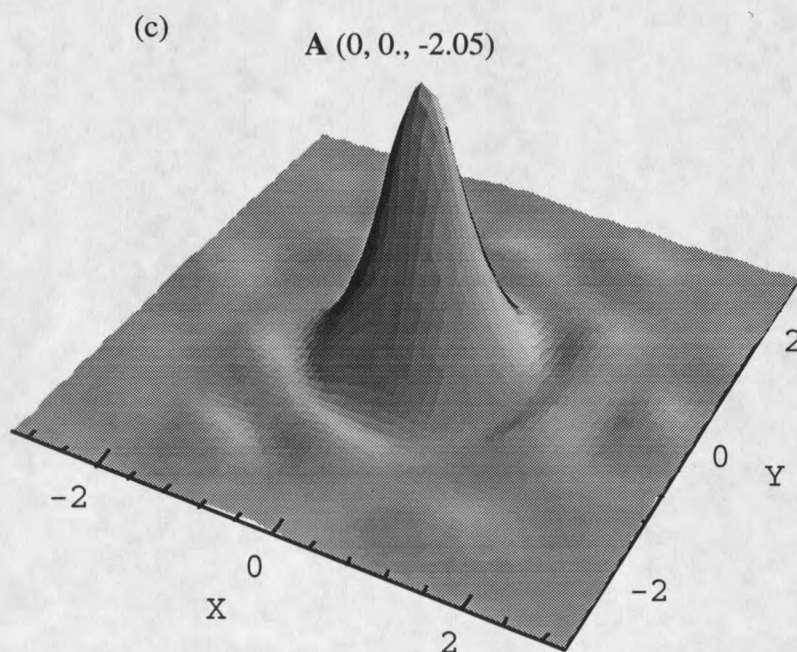


Fig. 5.13 (a)-(b) One-dimensional x-, y-scan passing through spot 'A' and (c) xy plane cut at $z = -2.05\text{\AA}$ at RT.



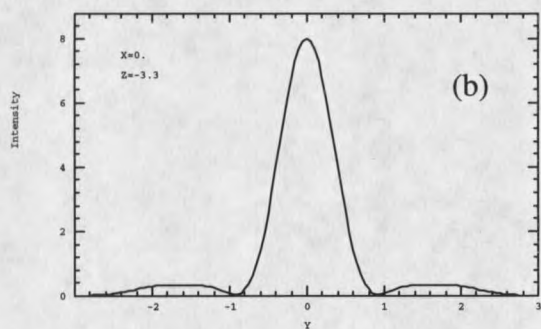
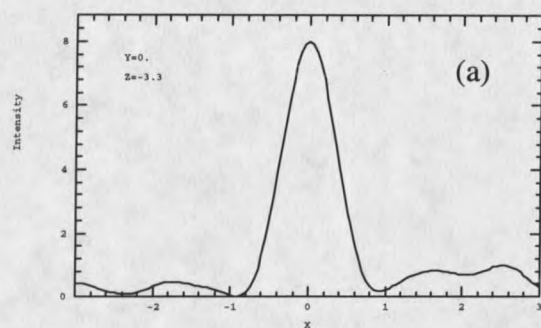
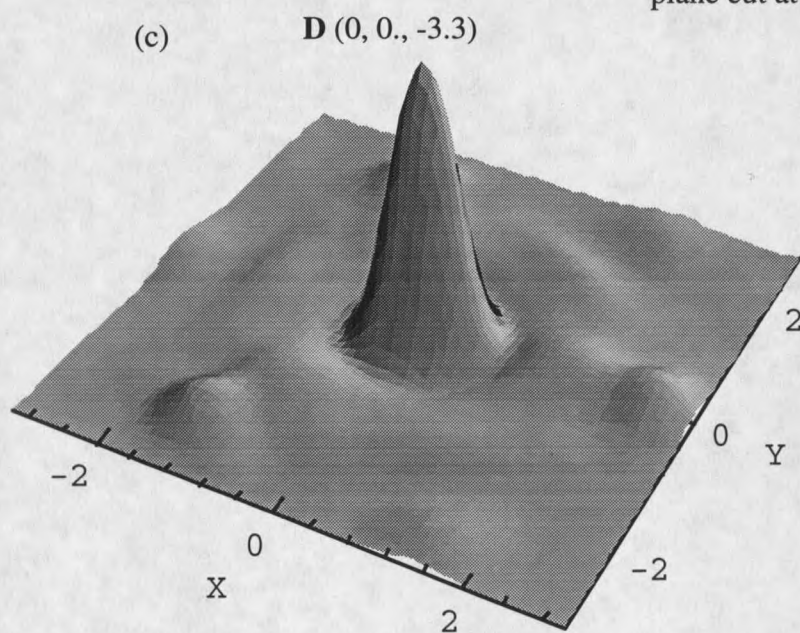


Fig. 5.14 (a)-(b) One-dimensional x-, y-scan passing through spot 'D' and (c) xy plane cut at $z = -3.3 \text{ \AA}$ at RT.



of spot 'A', and the other involves replacing the surface Ga, "the replacing site", as the image at (0., 0., -3.3) Å of spot 'D'. Spot 'B' seen at a depth of 2.9 Å below the Al emitter could be the second layer nitrogen atom from the on-top site, or a second layer Ga atom from the replacing site. We will clarify this issue after considering the images obtained from an annealed Al/GaN(0001) system.

Now we come back to discuss the two shoulders shown in the 1-D z scan of Fig. 5.12. By employing the same Photoelectron Diffraction Imaging (PDI) analysis parameters, except for omitting low k value contributions to the normalized diffraction spectra $\chi_k(k)$ functions, the two shoulders in the 1-D z-scan (Fig. 5.12) are almost totally gone. Fig. 5.16(a) shows an xz plane cut at $y = 0.0$ Å, with k ranging from 3.5 to 6.5 Å⁻¹ (before $k = 2.5$ -6.5 Å⁻¹). The image thus obtained is about the same as before (see Fig. 5.11), except that the relative image intensity at spot 'D' is smaller now (Fig. 5.16(a)). Note that spot 'D' is the next-next nearest neighbor in the replacing model (see Fig. 5.5, Al(2)). A larger photoelectron mean free path λ_e would be needed to give diffraction information originating from there. The smaller k value of 2.5 Å⁻¹ corresponds to a kinetic energy of about 25 eV, and thus corresponds to a larger λ_e value from the universal curve. The Fourier-like transform over the k range excluding the smaller values of k thus has less contributions from scatterers further away from the emitter, which explains the smaller relative image intensity of spot 'D'. Therefore, omitting the smaller values of k reduced the artifacts, as is shown in the one-dimensional z-scan in Fig. 5.16(b).

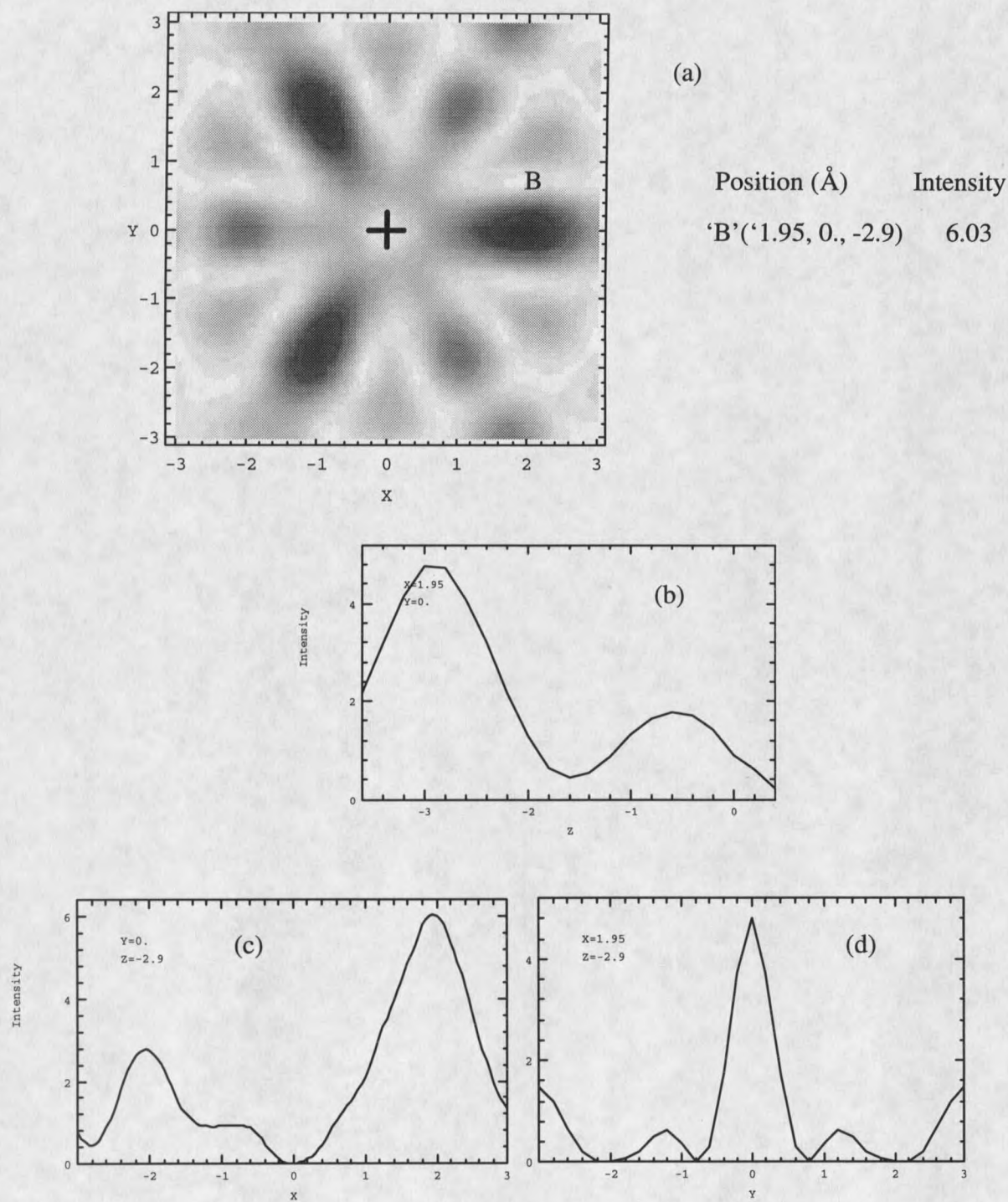
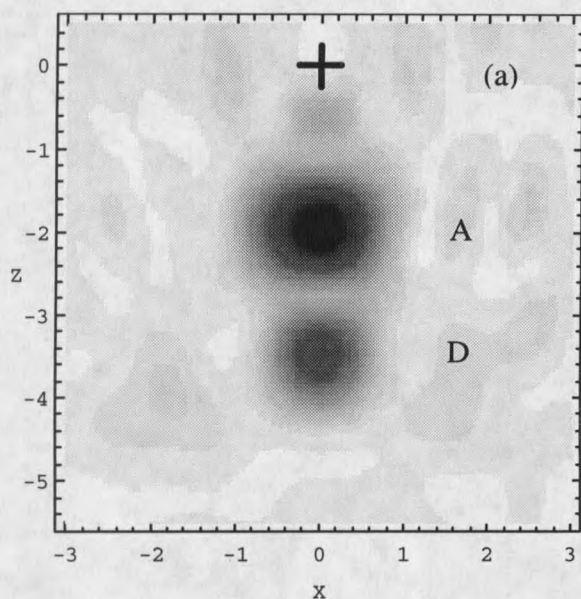


Fig. 5.15 (a) xy plane cut at $z = -2.9 \text{\AA}$ and (b)-(d) one-dimensional x -, y -, z -scan passing through spot 'B' at RT.



(a) xz plane cut at $y = 0.0 \text{ \AA}$

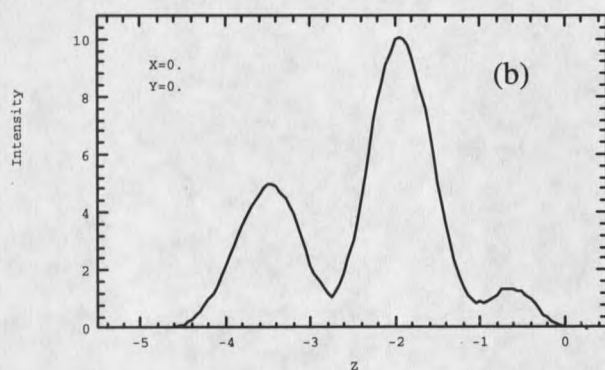
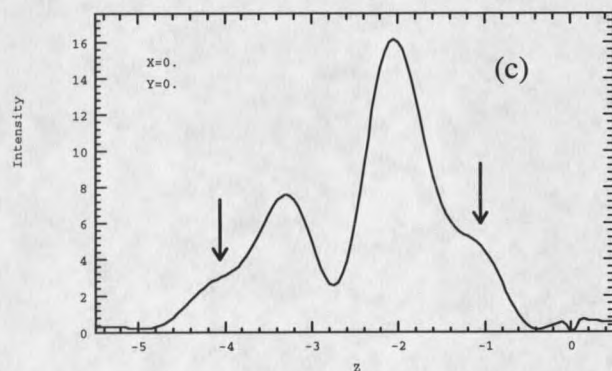


Fig. 5.16 (a) xz plane cut at $y=0.0 \text{ \AA}$ with $k=3.5-6.5 \text{ \AA}^{-1}$ (before $k=2.5-6.5 \text{ \AA}^{-1}$) and (b)-(c) the corresponding one dimensional scan along z axis passing through spot 'A' and 'D' at RT.

(b) One dimensional scan along z axis passing through atom 'A' and 'D' at RT, $k=3.5-6.5 \text{ \AA}^{-1}$.



(c) One dimensional scan along z axis passing through atom 'A' and 'D' at RT, $k=2.5-6.5 \text{ \AA}^{-1}$.

Al-(1×1)GaN(0001) after annealing

The previous Al-(1×1)GaN(0001) room temperature (RT) system was annealed to about 950°C for 10-15 seconds a few times and maintained a good (1×1) LEED pattern. Some representative CIS spectra, each plotted together with their smooth background $I_0(k)$ (chosen by spline fit), are shown in Fig. 5.17 for the annealed system.

Similar to the RT Al-(1×1)GaN(0001) system, Fig. 5.18 shows a xz plane cut at $y = 0.0 \text{ \AA}$ for Al-(1×1)GaN(0001) after annealing. The cross represents the Al emitter at the origin. Two strong image spots are again clearly seen, spot 'A' located at $(0., 0., -2.15) \text{ \AA}$ with an intensity of 10.1 and spot 'D' located at $(0., 0., -3.4) \text{ \AA}$ with an intensity of 7.9. Notice the much higher relative intensity of spot 'D', which has doubled its intensity as compared to the RT case (Fig. 5.11). Fig. 5.19 shows the one-dimensional z-scan passing through spots 'A' and 'D' after annealing. Again in addition to the two main intensity peaks corresponding to spots 'A' and 'D' in the one-dimensional z-scan, two shoulders at about $z = -1.2 \text{ \AA}$ and $z = -4.2 \text{ \AA}$, respectively, can be seen from Fig. 5.19. These are also due to artifacts related to multiple scattering at low k values, as has been discussed before.

Fig. 5.20(a), (b) and Fig. 5.21(a), (b) show the one-dimensional x-, y-, and z-scans passing through spots 'A' and 'D', with the xy plane cut (Fig. 5.20(c)) at $z = -2.15 \text{ \AA}$ (spot 'A') and (Fig. 5.21(c)) at $z = -3.4 \text{ \AA}$ (spot 'D'), respectively. The one-dimensional scans in Figures 5.20(a), (b) and Fig. 5.21(a), (b) again all show a typical FWHM $\leq 1 \text{ \AA}$. From the xz plane cut shown in Fig. 5.18, apart from the two strong image

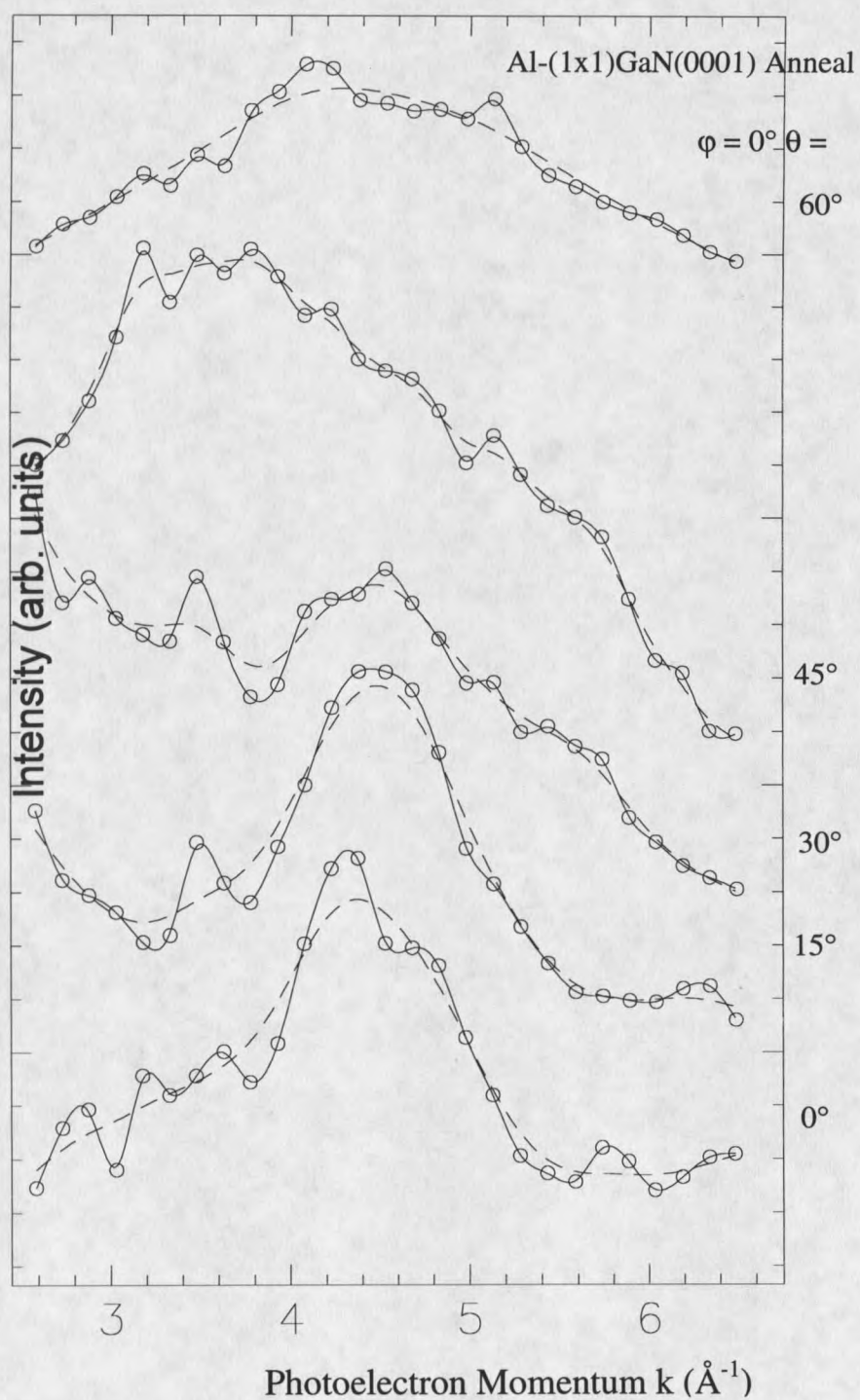


Fig. 5.17 Some representative CIS spectra (solid lines), each plotted together with their smooth background $I_0(k)$ (dashed lines) chosen by spline fit.

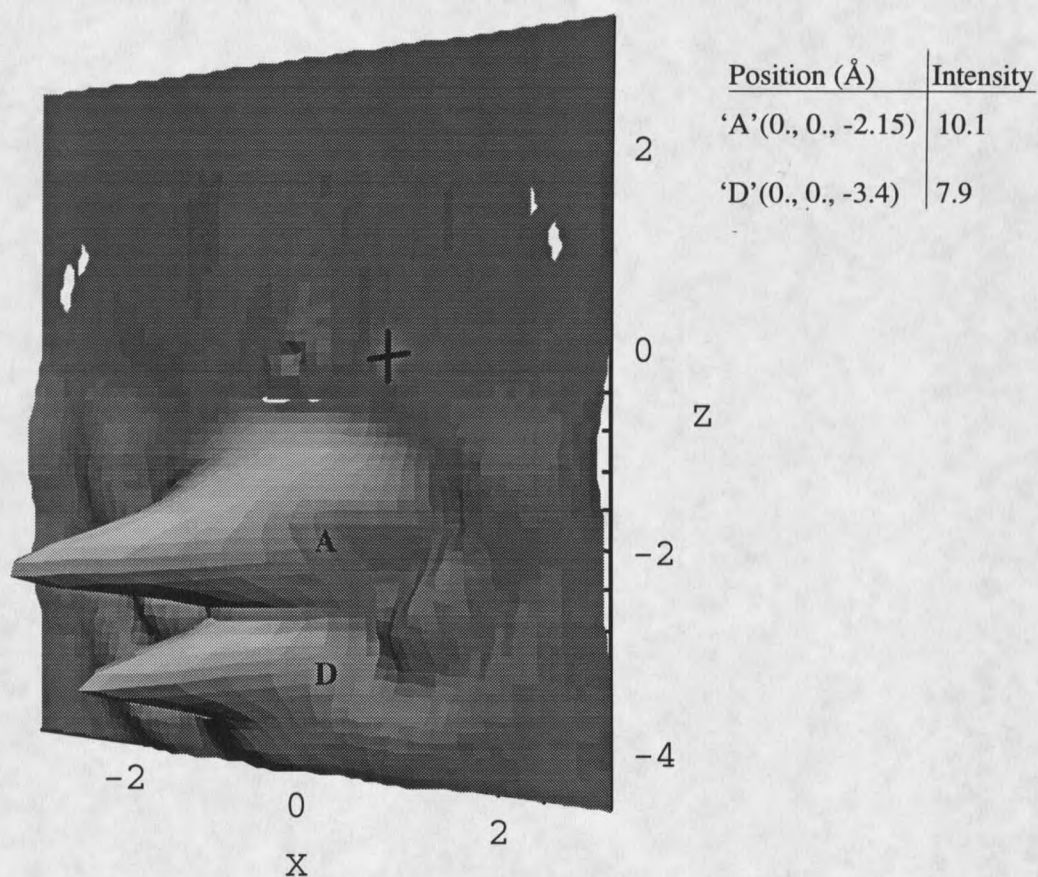


Fig. 5.18 (a) xz plane cut at $y=0.0\text{\AA}$ for Al-(1 $\times$ 1)GaN(0001) after annealing. The cross represents the Al emitter.

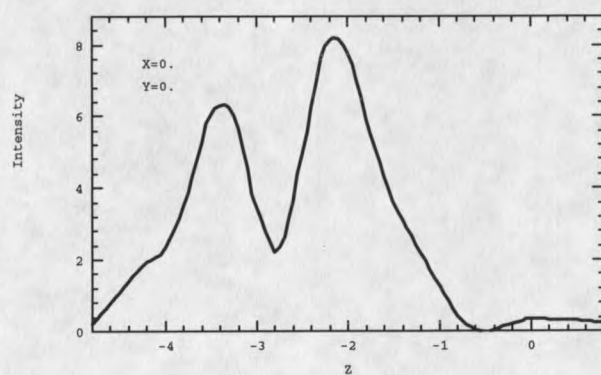


Fig. 5.19 One dimensional z-scan passing through spot 'A' and 'D' after annealing.

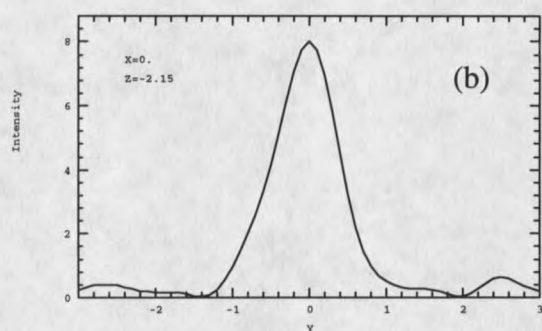
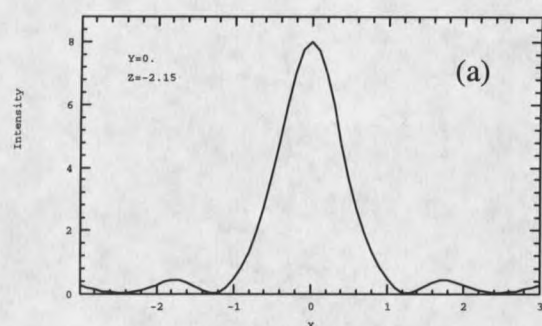
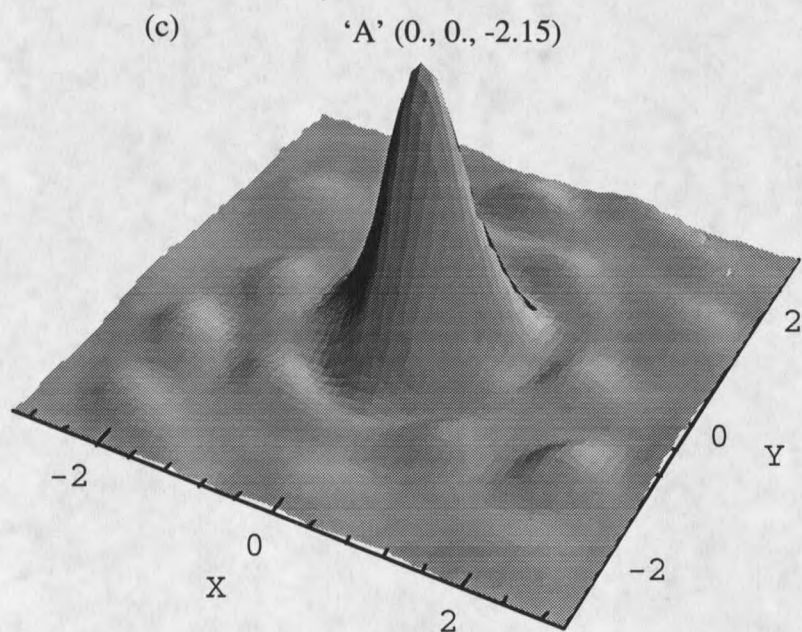


Fig. 5.20 (a)-(b) one-dimensional x- and y-scan passing through spot 'A', and (c) xy plane cut at $z = -2.15$ Å after annealing.



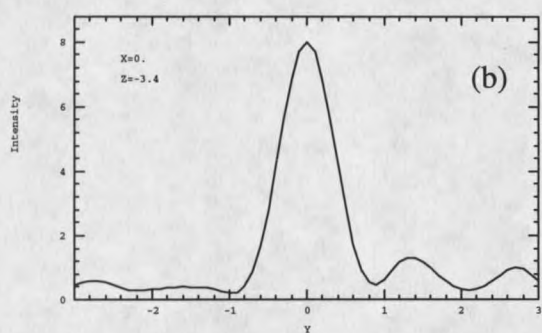
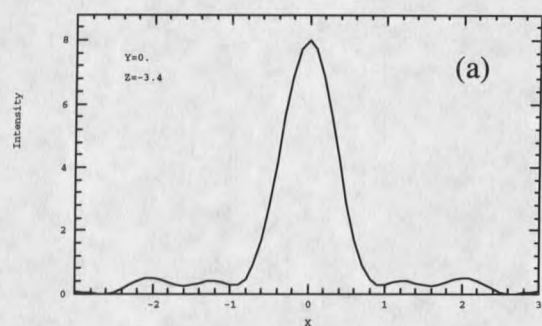
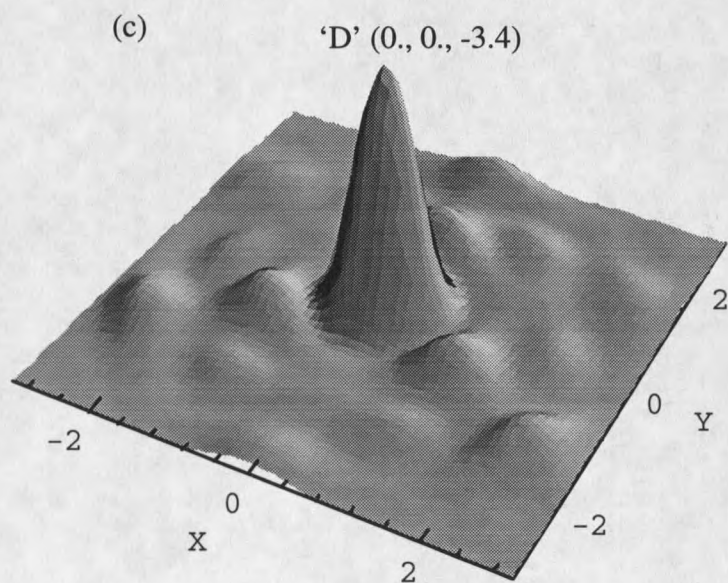


Fig. 5.21 (a)-(b) one-dimensional x-and y-scan passing through spot 'D', and (c) xy plane cut at $z = -3.4 \text{ \AA}$ after annealing.



spots right below the Al emitter, again no image signal is observed with intensity greater than background at off sample normal directions (on the side). This is due to the same reasons as explained for the room temperature system.

In order to utilize the data in a more appropriate way, we again analyzed the data using only part of the CIS spectra, with a CIS angular mesh consisting of $\theta = 52.5^\circ$ - 67.5° and $\phi = 0^\circ$ - 60° . The image thus obtained again showed a strong intensity spot at off normal directions. Fig. 5.22(a) shows a xy plane cut at $z = -2.83 \text{ \AA}$. The spot 'B' located at $(1.8, 0., -2.83) \text{ \AA}$ has an image intensity of 10.2. Fig. 5.22(b)-(d) also show the one-dimensional x-, y-, and z-scan passing through spot 'B'. The elongated image is again due to the relatively smaller number of CIS's taken into account in the transformation.

In a similar way as used for the RT system, we come back to study the two shoulders shown in the one-dimensional z-scan of Fig. 5.19. By employing the same PDI analysis parameters except omitting low k value contributions to the normalized diffraction spectra $\chi_k(k)$ functions, the two shoulders in the one-dimensional z-scan are again almost totally gone.

Fig. 5.23(a) shows an xz plane cut at $y = 0.0 \text{ \AA}$, with k range from 3.5 to $6.5 \text{ \AA}^{-1}$ (before $k = 2.5$ - $6.5 \text{ \AA}^{-1}$). The image thus obtained is approximately the same as before, except that the relative image intensity at spot 'D' is smaller now (compare to Fig. 5.18). Again this is because spot 'D' is the next-next nearest neighbor in the replacing model. A larger photoelectron mean free path λ_e would be needed to give diffraction information originating from there. By omitting the smaller values of k the artifacts are weaker, as is

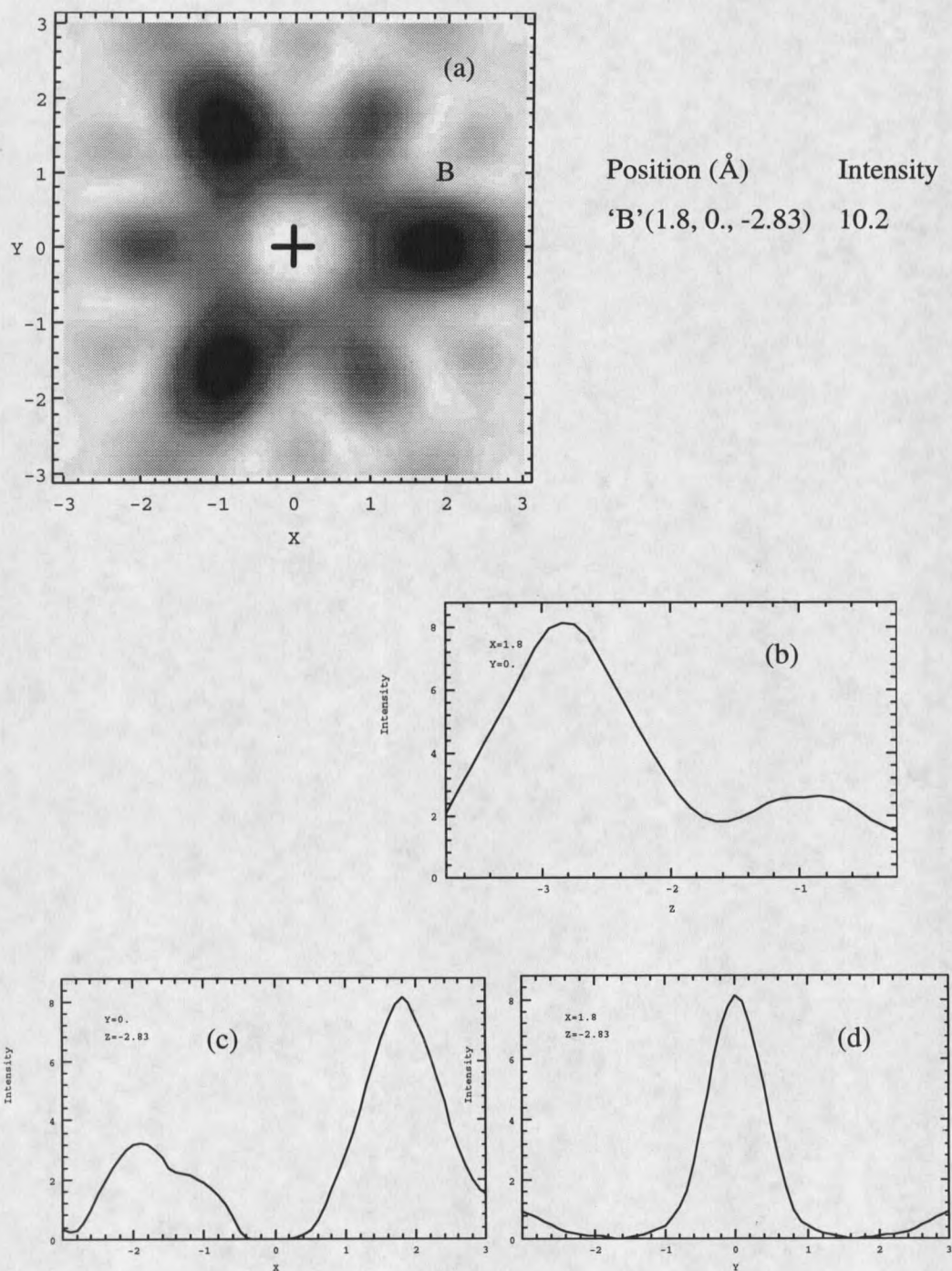


Fig. 5.22 (a) xz plane cut at $z = -2.83 \text{ \AA}$ and (b)-(d) one-dimensional x -, y -, z -scan passing through spot 'B' after annealing.

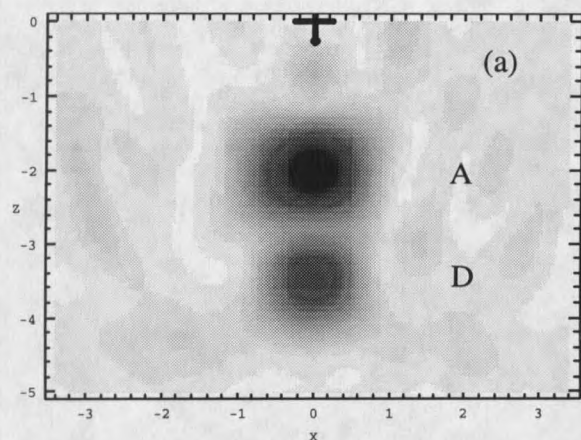
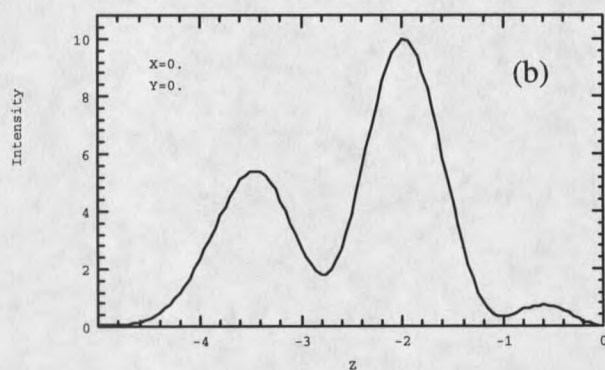
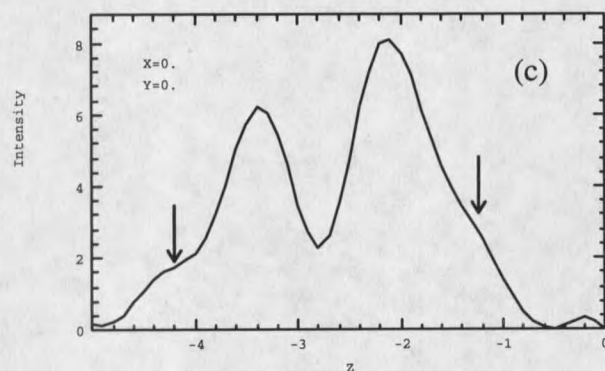


Fig. 5.23 (a) xz plane cut at $y=0.0 \text{ \AA}$, with $k=3.5\text{-}6.5 \text{ \AA}^{-1}$ (before $k=2.5\text{-}6.5 \text{ \AA}^{-1}$) and (b) the corresponding one-dimensional scan along the z axis passing through spot 'A' and 'D' after annealing.



(b) One dimensional z -scan passing through atom 'A' and 'D' after annealing. $k=3.5\text{-}6.5 \text{ \AA}^{-1}$.



(c) One dimensional z -scan passing through atom 'A' and 'D' after annealing. $k=2.5\text{-}6.5 \text{ \AA}^{-1}$.

shown in the one-dimensional z-scan in Fig. 5.23(b).

By comparing the images obtained from both RT and annealed Al-(1×1)GaN(0001) systems, the much higher image intensity of spot 'D' (0.0, 0.0, -3.4) Å for the annealed system indicates that the Al replacing site is more favorable upon annealing. The stronger image signal from spot 'B' at (1.8, 0.0, -2.83) Å for the annealed system indicates that it is associated with the replacing site, i.e., it is the second layer gallium in the replacing site model rather than the second layer nitrogen in the on-top site model. The larger atomic number of Ga would also give rise to a larger scattering effect from Ga scatterers than that from N scatterers.

Thus we postulate a model with two in-equivalent Al adsorption sites, as depicted in Fig. 5.24. One is directly above the surface Ga atom, the on-top site (Fig. 5.24(a)), and the other is replacing the surface Ga (Fig. 5.24(b)), with the replacing site more favorable for the annealed system. Spot 'B' at a depth of about 2.83 Å below the Al emitter (Fig. 5.22(a)) is the second layer Ga atom associated with the replacing site.

To summarize the above results, Table 5.1 lists the three-dimensional atomic positions and image intensity of GaN(0001)(1×1)-Al (RT and after annealing) obtained from the PDI technique, and a comparison to the estimated positions obtained from bulk wurtzite GaN lattice constants. The Al emitter is located at the origin, with the Z axis along [0001], the X axis along $[10\bar{1}0]$ and the Y axis along $[1\bar{2}10]$. All units in the table are in Å.

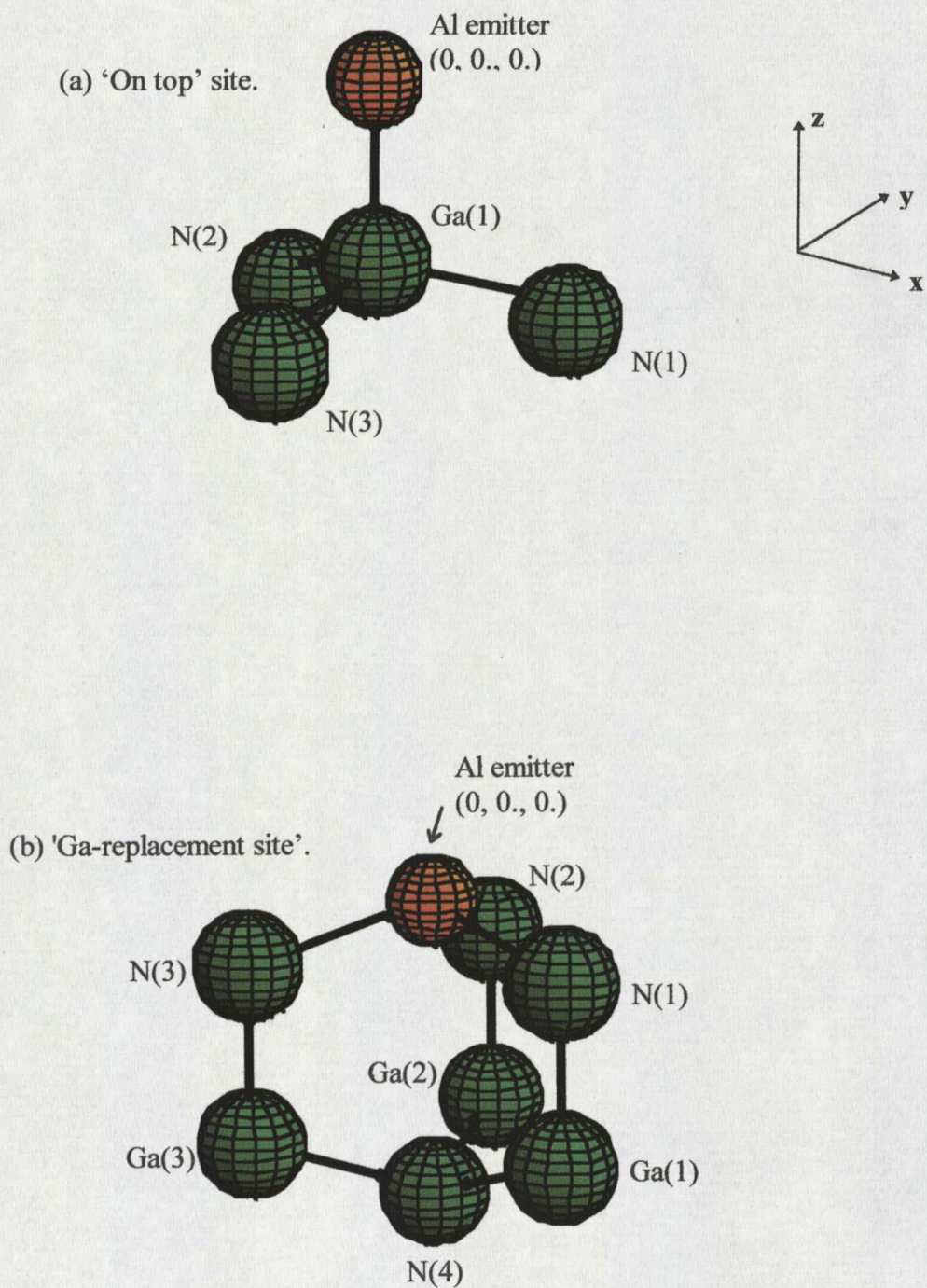


Fig. 5.24 Two inequivalent Al adsorption sites, (a) the 'On top' site and (b) the 'Ga-replacement site'.

Table 5.1 Three-dimensional atomic positions and image intensities of GaN(0001)(1×1)-Al (RT and after anneal) obtained from the PDI technique and comparisons to the estimated positions obtained from bulk wurtzite GaN lattice constants. The Al emitter is located at the origin. (a) The Al emitter *at on-top site and* (b) the *replacing site*. All units in the table are in unit of Å.

(a) “on-top site”

Ga or N atoms (on top site)	corresponding layer and depth	atomic positions (this experiment)	image intensity	Estimates from bulk
Ga(1)(Fig.5.24(a)) or atom ‘A’ in the images	1st layer	atom ‘A’ ^a :	atom ‘A’ ^a :	NA
	2.05 Å RT	(0,0,-2.05) RT	10.0 RT	
	2.15 Å ANN	(0,0,-2.15) ANN	10.1 ANN	

(b) “Ga-replacement site”

Ga or N atoms (replace site)	corresponding layer and depth	atomic positions (this experiment)	image intensity	Estimates from bulk
Ga(1) (Fig.5.24(b)) or atom ‘B’ in the images	2nd layer	atom ‘B’ ^b :	atom ‘B’ ^b :	(1.84,0,-2.6)
	2.9 Å RT	(1.95,0,-2.9) RT	6.03 RT	
	2.83 Å ANN	(1.8,0,-2.83) ANN	10.2 ANN	
N(4) (Fig.5.24(b)) or atom ‘D’ in the images	3rd layer	atom ‘D’ ^a :	atom ‘D’ ^a :	(0,0,-3.24)
	3.3 Å RT	(0,0,-3.3) RT	4.0 RT	
	3.4 Å ANN	(0,0,-3.4) ANN	7.9 ANN	

^a Atomic positions obtained from this experiment by utilizing all the CIS’s and transform over k from 2.5-6.5 Å⁻¹ by PDI technique.

^b Atomic positions obtained from this experiment by utilizing only part of the CIS’s ($\theta \geq 52.5^\circ$, $\phi = 0-60^\circ$) and transform over k from 3.5-6.5 Å⁻¹ by PDI technique.

CHAPTER 6

METAL-SEMICONDUCTOR INTERFACES OF Al/GaN(0001)

Experimental

Experiments were performed at the University of Wisconsin-Madison Aladdin storage ring on the Iowa-Montana State ERG/Seya monochromator beamline. The 2 meter ERG provides high flux and high energy resolution in the photon energy ($h\nu$) range from 37.5 to 240 eV, and the 5 meter ERG in the photon energy range from 250 to 1200 eV. The Seya monochromator provides high flux and good energy resolution, typically <100 meV, in the photon energy range of 14-40 eV which is very convenient for valence band work. The details of the ERG/Seya monochromator are reported elsewhere.⁷² The main chamber includes a LEED system and a double-pass cylindrical mirror analyzer (CMA) with a retractable angle-resolving drum.

The contamination of the surface was checked by choosing $h\nu$ to be surface sensitive. Photoemission measurements of C 1s are taken at $h\nu = 350$ eV and O 1s at $h\nu = 610$ eV, as well as valence band spectroscopy for the O 2p resonance.

A heavily doped n^+ -GaN(0001) ($2 \times 10^{19} \text{ cm}^{-3}$) sample was used to minimize charging and photovoltaic effects. The p-type sample has a doping level of $1 \times 10^{17} \text{ cm}^{-3}$ and is, thus, susceptible to possible surface charging or photovoltaic effects.

The Al was evaporated from a basket made with three strands of twisted tungsten wire at a pressure of less than 2×10^{-9} Torr in the main (measurement) chamber which has an operating base pressure of 1.3×10^{-10} Torr. Al deposition was monitored by a quartz-crystal oscillator (QCO) during evaporation. Each experiment was conducted in less than 12 hours in order to minimize carbon and oxygen contamination, which was minimal, as checked by the surface sensitive photoemission spectroscopy.

The overall resolution (monochromator and spectrometer) is 120 meV, 170 meV and 1.1 eV for Ga 3d, Al 2p and N 1s respectively. All the results are normalized to the photon flux measured by a tungsten mesh placed between the monochromator and the sample.

Growth Mode^{67,94} and LEED STUDY

For the simplest layer by layer growth (FM mode), we assume a continuum-type description of the change of the photoemission line intensity dI . dI is then related to the change of overlayer thickness dx by:

$$dI/I = -dx/\lambda \quad (6-1)$$

where λ is the electron mean free path and x the overlayer thickness. Thus an exponential decay of the intensity occurs as the overlayer thickness increases. The decay (for only completed whole overlayers) is :

$$I^F/I_\infty^F = 1 - \exp(-\theta' d_\perp/\lambda) \quad (6-2)$$

where I_∞^F is the intensity measured on the bulk overlayer material, θ' is the number of

monolayers deposited, and $d_{\perp}$ is the thickness of a monolayer. The thickness $d_{\perp}$ is divided by a $\cos\theta$ factor, with $\theta = 42^\circ$, the mean acceptance angle of the CMA analyzer.

The intensity originating from the substrate is then:

$$I^S/I_0^S = \exp(-\theta'd_{\perp}/\lambda) \quad (6-3)$$

where I_0^S is the intensity of the substrate without any overlayer deposition.

The attenuation curve is obtained by subtracting a polynomial background, normalizing the count rate to the photon flux, as read from the tungsten mesh current at the beginning of each scan, and then integrating the area under the background subtracted peaks. The attenuation of the Ga 3d bulk and N 1s core levels, normalized to the photon flux, is shown as a function of increasing Al coverage in Fig. 6.1, where one monolayer (ML) is defined as one Al atom per GaN surface lattice site. From the wurtzite GaN lattice constant, 1 ML is equivalent to $1.14 \times 10^{15} \text{ cm}^{-2}$ for the GaN basal plane, and from the Al mass density, a QCO thickness of 1 Å Al is equivalent to $6.02 \times 10^{14} \text{ cm}^{-2}$. Therefore, 1 ML is $\sim 1.89 \text{ Å}$.

In the first two monolayers of Al deposition, the N 1s total signal is attenuated at a slower rate than that of the Ga 3d bulk (Fig. 6.1). The electron mean free path λ obtained from Fig. 6.1 and equation (6-3) for the Ga 3d bulk and N 1s core-levels are 2.94 and 8.46 Å, respectively.

There are several explanations as to why the Ga/N ratio decreases with Al coverage. First, the photon energy used for the N 1s core is 500 eV, which corresponds to N 1s emission at kinetic energy around 99 eV, as compared to the Ga 3d emission at kinetic energy about 45 eV. The higher photoelectron kinetic energy thereby gives rise to a larger

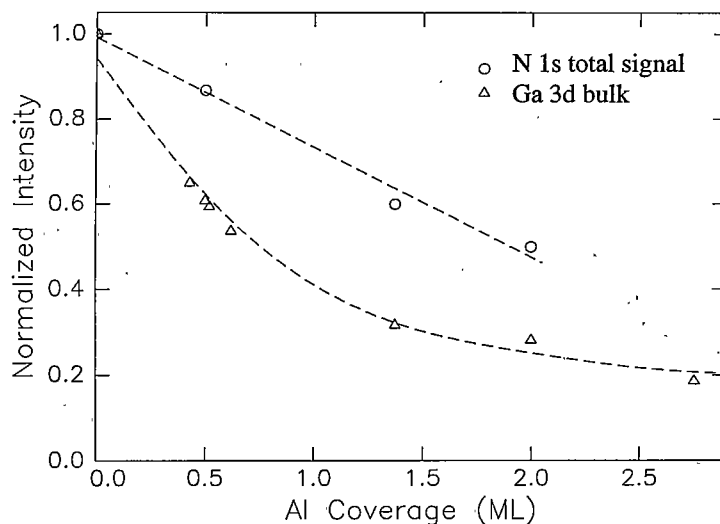


Fig. 6.1 The attenuation of bulk Ga 3d and N 1s core levels with the increasing Al overlayer thickness. The intensity is normalized to the clean surface and photon flux.

value of the electron mean free path λ .

The empirical relation between the electron mean free length λ and the kinetic energy of the photoelectrons E (eV) is:⁹⁵

$$\lambda(\text{\AA}) = 1430 E^{-2} + 0.54 E^{1/2} \quad (6-4)$$

Taking $E = 45$ eV and 99 eV for Ga 3d and N 1s photoelectrons, the corresponding λ 's for Ga 3d bulk and N 1s core-levels are 4.3 and 5.5 $\text{\AA}$, respectively. The slower attenuation of the N 1s core level, as a function of Al coverage, can not therefore be exclusively due to the larger λ value of the N 1s, as indicated by the comparison of the above estimated λ values.

Another possible reason why the attenuation rates of Ga 3d bulk and N 1s are different could be that there is a preferential N outdiffusion, or excessive nitrogen related defects (such as N antisites) near the immediate interface, which may lead to the decrease of the Ga/N signal at higher Al coverage.

LEED studies showed that the 1×1 LEED pattern persists with an increasing background until Al coverage of about 3 ML. The persistence of the LEED pattern suggests cluster formation. The LEED study and the attenuation of the bulk Ga 3d signal both suggest a modified Stranski-Krastanov^{96,97} growth mode. Therefore we conclude that the growth morphology is two dimensional only in the first one-half to one monolayer, then clusters (islands) form at higher coverage.

Band Bending and Surface Fermi Level Movement

Changes in band bending were measured as a function of Al coverage for both n^+ - and p-type GaN to monitor trends in the surface semiconductor Fermi level position within the band gap. The surface Fermi level of clean n^+ -type GaN(0001) is pinned in the gap above the valence band maximum (VBM) by about 2 eV, indicating an initial band bending of 1.45 eV, if we assume that the forbidden band gap E_g of GaN is 3.4 eV ($eV_d = E_c - E_f \approx -0.05$ eV for $n = 2 \times 10^{19} \text{ cm}^{-3}$, and take $m_e^* = 0.236m_0$), as depicted in Fig. 6.2. The surface Fermi level of the clean p-type GaN is pinned in the gap above the VBM by about 1 eV, indicating an initial band bending of 0.87 eV (take $E_g = 3.4$ eV, $eV_a = E_f - E_v \approx 0.13$ eV for $p = 1 \times 10^{17} \text{ cm}^{-3}$, and $m_h^* = 0.8m_0$).

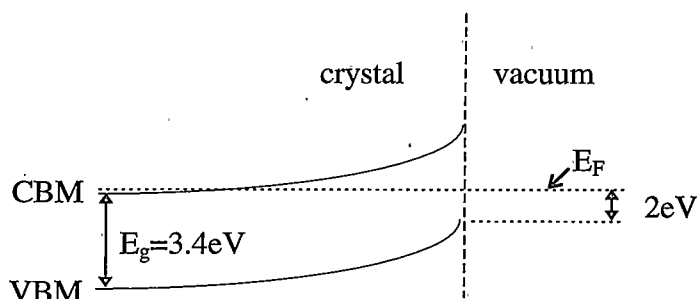


Fig. 6.2 Schematic drawing of an initial upward band bending on the clean surface.

The surface Fermi level often changes during the initial stage of interface formation, due to the formation of new gap states.⁹⁸ Fig. 6.3 shows the Ga 3d core-level energy distribution curve (EDC) at different Al coverage on n^+ -type GaN(0001). The horizontal axis is the photoelectron kinetic energy relative to the vacuum level of the photoelectron spectrometer. Since the spectrometer has a constant work function, the change of the photoelectron kinetic energy peak position corresponds to a change in the binding energy relative to the Fermi level. The nontrivial change of the Ga 3d core line shape, with increasing Al coverage, indicates the relatively strong interactions at the Al-GaN interface. From Fig. 6.3 it is seen that the Ga 3d core-level shifts to lower kinetic energy in the first half ML of Al coverage and stays about the same for Al coverage above 1.5 ML.

Since the bulk core level binding energy is tied to the VBM, the initial shift in kinetic energy indicates movement of the Fermi level relative to the VBM. The surface

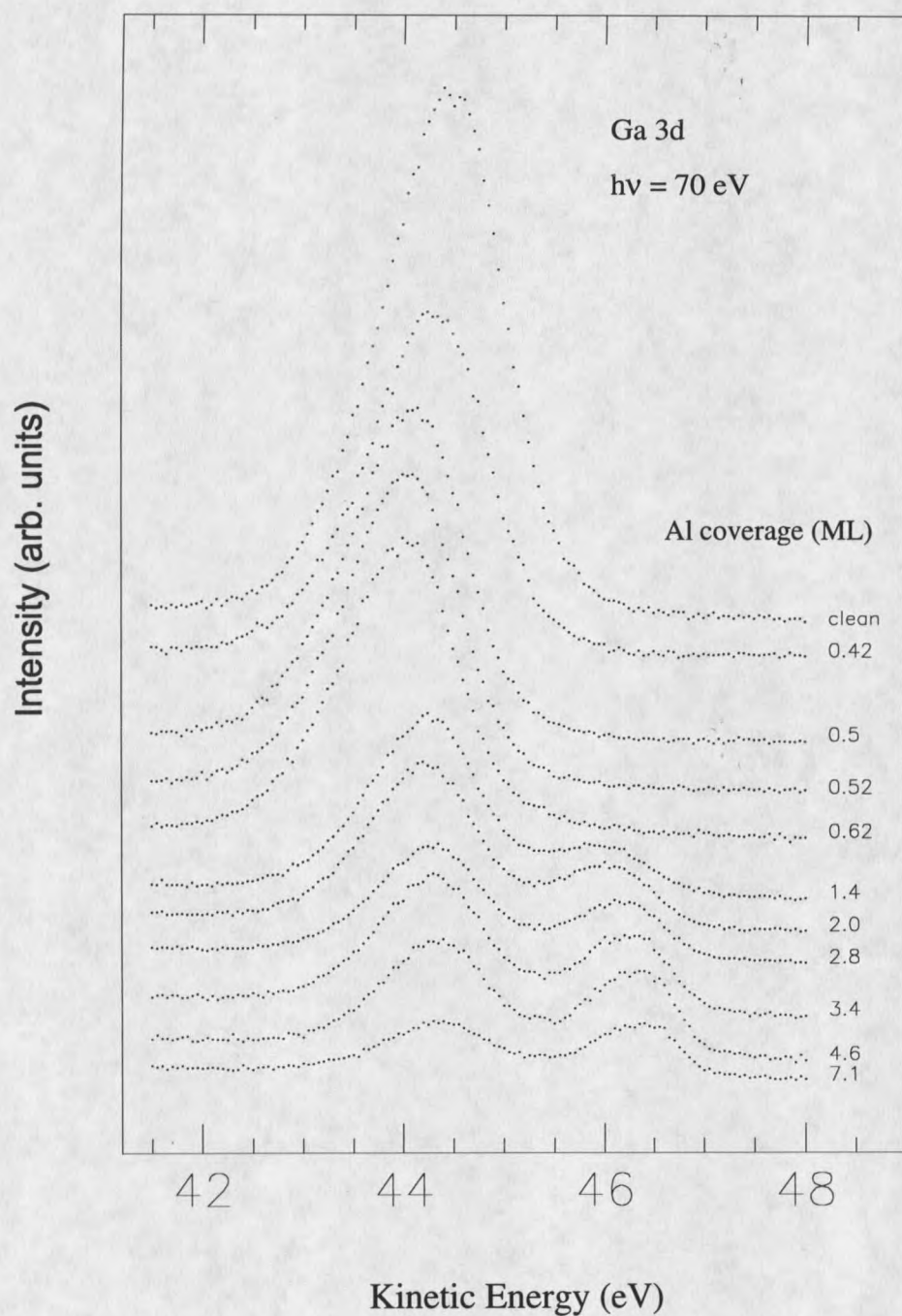


Fig. 6.3 Ga 3d core-level EDC curves taken as a function of Al coverage. The kinetic energy is relative to the vacuum level of the spectrometer.

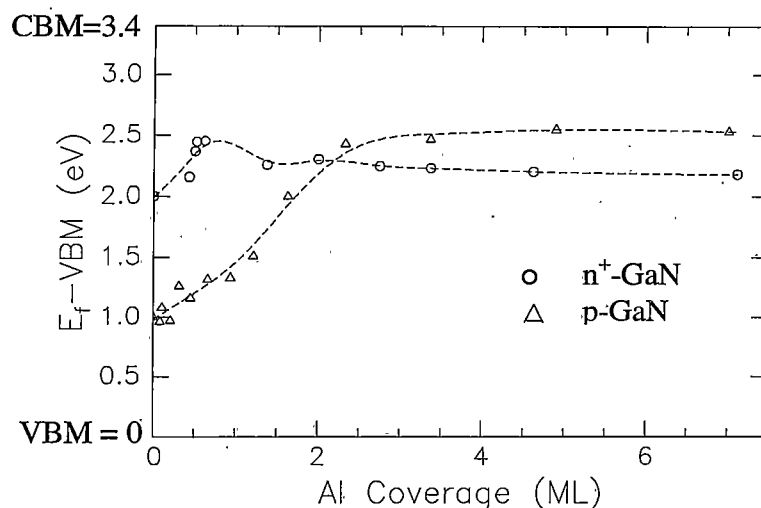


Fig. 6.4 The surface Fermi level movement with the Al coverage for both n^+ - and p-type GaN obtained from the bulk Ga $3d_{5/2}$ core level position of the Voigt fit.

Fermi level movement with the Al coverage is shown in Fig. 6.4 for both n^+ - and p-type GaN obtained from the bulk Ga $3d_{5/2}$ core level position of the Voigt (convolution of Gaussian and Lorentzian) fit. For n^+ -type GaN the Fermi level moves initially further away from the VBM (circles in Fig. 6.4), resulting in less upward band bending, then stays about the same at 2.2 eV above the VBM after Al coverage above 1 ML. For p-type GaN the Fermi level also moves initially further away from the VBM (triangles in Fig. 6.4), resulting in more downward band bending, and then stays about the same at 2.5 eV above the VBM after Al coverage above 2 ML.

It is unlikely that the initial shift of the bulk Ga $3d_{5/2}$ core level position is due to a chemical bond shift because such a shift should not saturate before completion of the first

monolayer of the adsorbate. Furthermore, this initial shift can not be due to sample charging, since in that case, the Ga 3d core-level peak position should shift to higher kinetic energy with increasing Al overlayer thickness which diminishes any charging effect. Thus, it is concluded that the Ga 3d core-level peak shift is due to band bending, as also confirmed from the rigid movement of the upper valence band to lower kinetic energy during the first half ML of Al coverage.

The N 1s core level emission is also recorded at a few layers of Al coverage. Unfortunately the 5-meter ERG grating flux, and monochromator resolution, is much worse than the 2-meter ERG grating. The N 1s core level emission shows up as a broad peak, which is decomposed into two peaks separated by ~ 2 eV, with FWHM of about 1.15 eV each. This leads to a bigger error for precise determination of the N 1s core position. Nevertheless the N 1s core emission shifts in the same sense as the Ga 3d core-level. It (N 1s) shifts to lower kinetic energy by about 0.4 eV at 1.4 and 2 ML of Al coverage as compared to the clean surface.

From the surface Fermi level movement within the band gap of n^+ - and p-type GaN (Fig. 6.4), it seems some donor defects are associated with the Fermi level pinning⁹⁹ (see defect model in chapter 2). Possible native donor defects in GaN are N vacancies, V_N , which lie about 40 meV below the CBM, and N antisites, N_{Ga} , which lie about 0.3-0.5 eV below CBM,⁵⁸ as shown schematically in Fig. 6.5.

The N related defects are especially possible when one considers the fact that all of the unintentionally doped GaN samples grown today are still n-type, i.e. the background doping is always n-type, despite the fact that the background electron concentration has

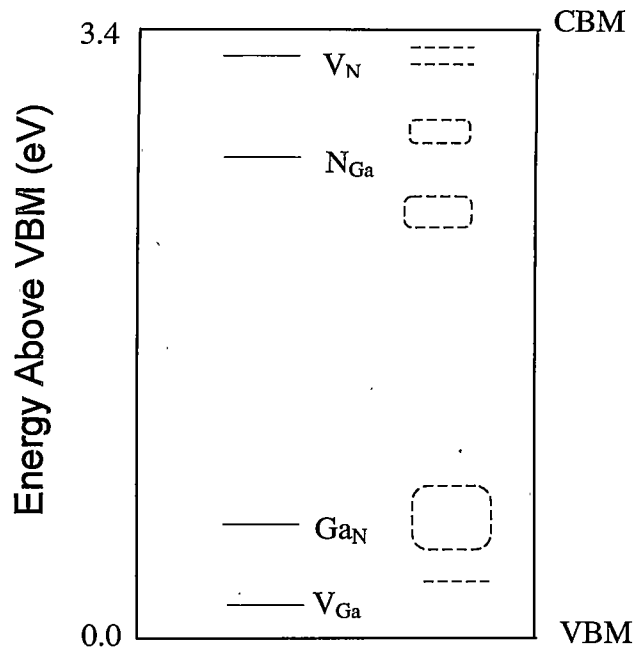


Fig. 6.5 Point defects in wurtzite GaN. The dashed line is experimental data and the solid line is the theoretical predictions.

been brought down from 10^{19} cm^{-3} to the mid 10^{16} cm^{-3} level now. Unanimous belief nowadays is that the N vacancies, which lie roughly 40 meV below the CBM (Fig. 6.5), are responsible for the electron background in GaN. An excess of N antisites, or N vacancies close to the interface could be produced by possible nitrogen outdiffusion and the sample cleaning procedure.

When acceptors and nitrogen donor defects are both present, compensation occurs, and the Fermi level should increase rapidly when the donor defect concentration, N_d , approaches the acceptor doping level N_a ; when N_d is much larger than N_a , E_f should come to rest at an energy intermediate between the acceptor and donor levels.²⁶ The undoped

sample we have has a background n-type doping of approximately 10^{16} cm^{-3} . The N related donor defect concentration could be larger than the doping level in the p-type GaN sample ($1 \times 10^{17} \text{ cm}^{-3}$). Thus we tentatively assign N antisites and N vacancies as being the donor defect states that pin the Fermi level. Due to the donor nature of the N related defects, this should push E_f up towards the CBM for both n- and p-type GaN.

The final surface Fermi level pinning position for the p-type sample is about 0.3 eV higher than that of n⁺-type GaN. Considering the lower doping level of the p-type sample ($1 \times 10^{17} \text{ cm}^{-3}$), there could be some photovoltaic effects¹⁰⁰ which would give an overestimate of the initial band bending on the metal free surface.^a In this case, the Fermi level in the gap, at all Al coverage, should move down toward the VBM by the amount of the correction due to the surface photovoltaic effects.

Chemical Shift

Experimental Results

Changes in chemical bonding causes charge redistribution near the interface and a resultant dipole which might affect the Schottky barrier height of the macroscopic junction. High resolution angle-integrated core-level photoemission allows chemical effects to be followed when the interface is formed. The surface sensitive core-level

^a The optical absorption by illumination can generate electron-hole pairs. If the semiconductor has an internal electric field, the radiation induced electron-hole pairs can be separated by the internal field to give rise to a voltage in an external circuit, the so-called photovoltaic effect. A lower sample doping level would have a larger depletion width, and thereby increase the photovoltaic effect.

photoemission of Ga 3d and Al 2p are fitted by least-square Gaussian-broadened Lorentzian (Voigt) functions, with each component split due to spin-orbit interactions.

The Ga 3d spin-orbit splitting and the branch ratio of Ga 3d_{5/2} to Ga 3d_{3/2} are obtained from the Voigt fit of the metallic component of Ga 3d for a thick Al overlayer on GaN. The spin orbit splitting of Ga 3d is found to be 0.44 eV and the branch ratio is 0.74 (close to $(2j_- + 1)/(2j_+ + 1) \approx 0.67$). These values are used consistently (as fixed parameters) for all the Ga 3d components at all Al coverage.

The Voigt fitting analysis of the Ga 3d and Al 2p core-level signals, with the photoelectron kinetic energy corresponding to the shortest mean free path (kinetic energy chosen at about 45 eV) was conducted for all Al coverage. The Ga 3d core-level decomposition required four components at Al coverage above 1 ML, as shown in Fig. 6.6. The attenuation of different components of Ga 3d with Al coverage is shown in Fig. 6.7.

The bulk Ga 3d (component 1) shows a fast, almost linear, decrease in intensity during the initial Al deposition (<1 ML) and attenuates much slower afterwards.

Component 2, decreases slowly with Al coverage. The intensity ratio of $I_2/(I_1 + I_2)$ decreases from about 21% on the metal free surface to about 12% at Al coverage of ~7 ML. The Voigt fit of Ga 3d conducted on the clean GaN surface requires this second component to be at 0.82 eV higher binding energy than that of the bulk Ga 3d_{5/2} in order to obtain a good fit. This is, thus, used for all of the Voigt fits, for various Al coverage, i.e. the energy shift relative to bulk Ga 3d_{5/2} is fixed at 0.82 eV.

The third Ga 3d component has a shift of 1.97 eV to lower binding energy as

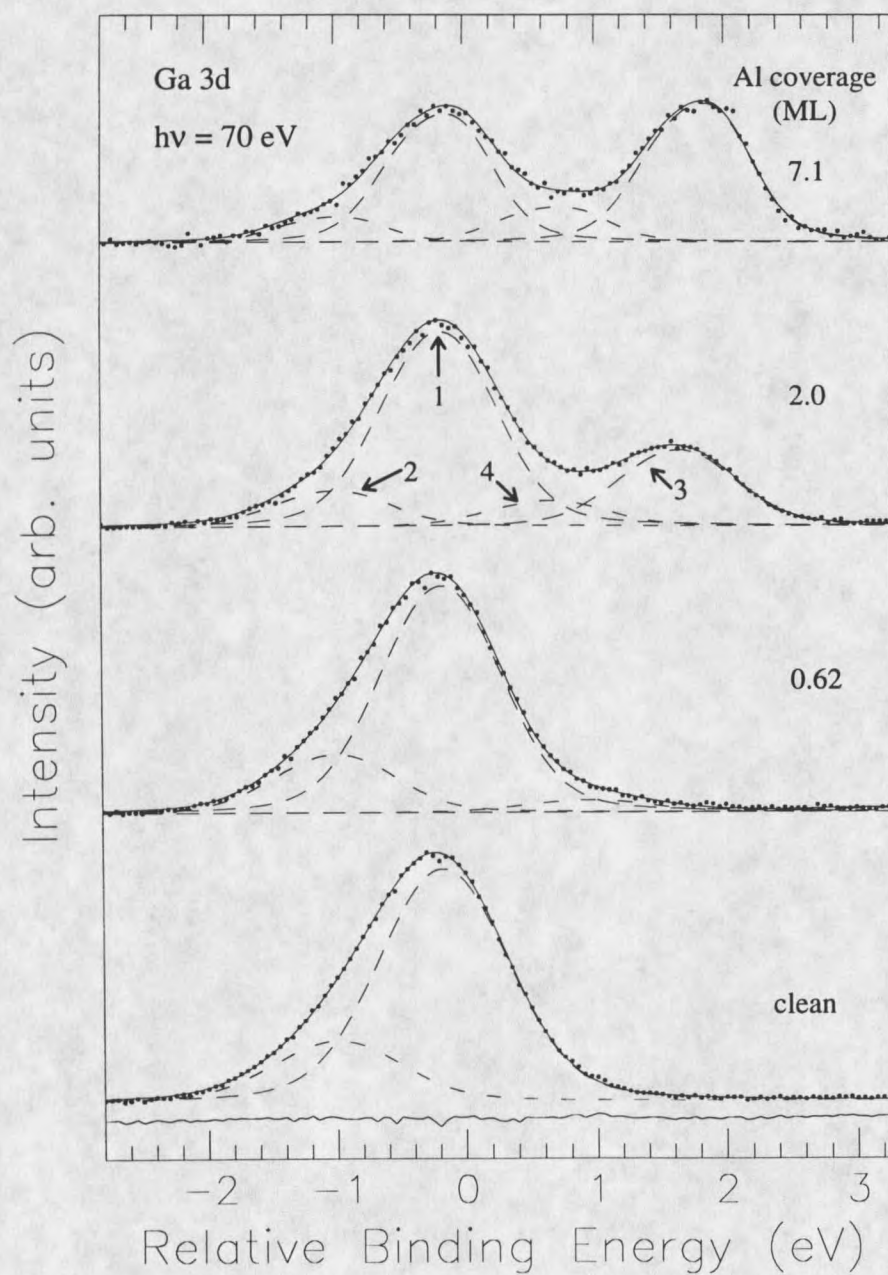


Fig. 6.6 Ga 3d core-level decomposition at different Al coverages obtained by Voigt fitting. The four components are labels as 1 to 4. Peak shifts due to band bending have been removed.

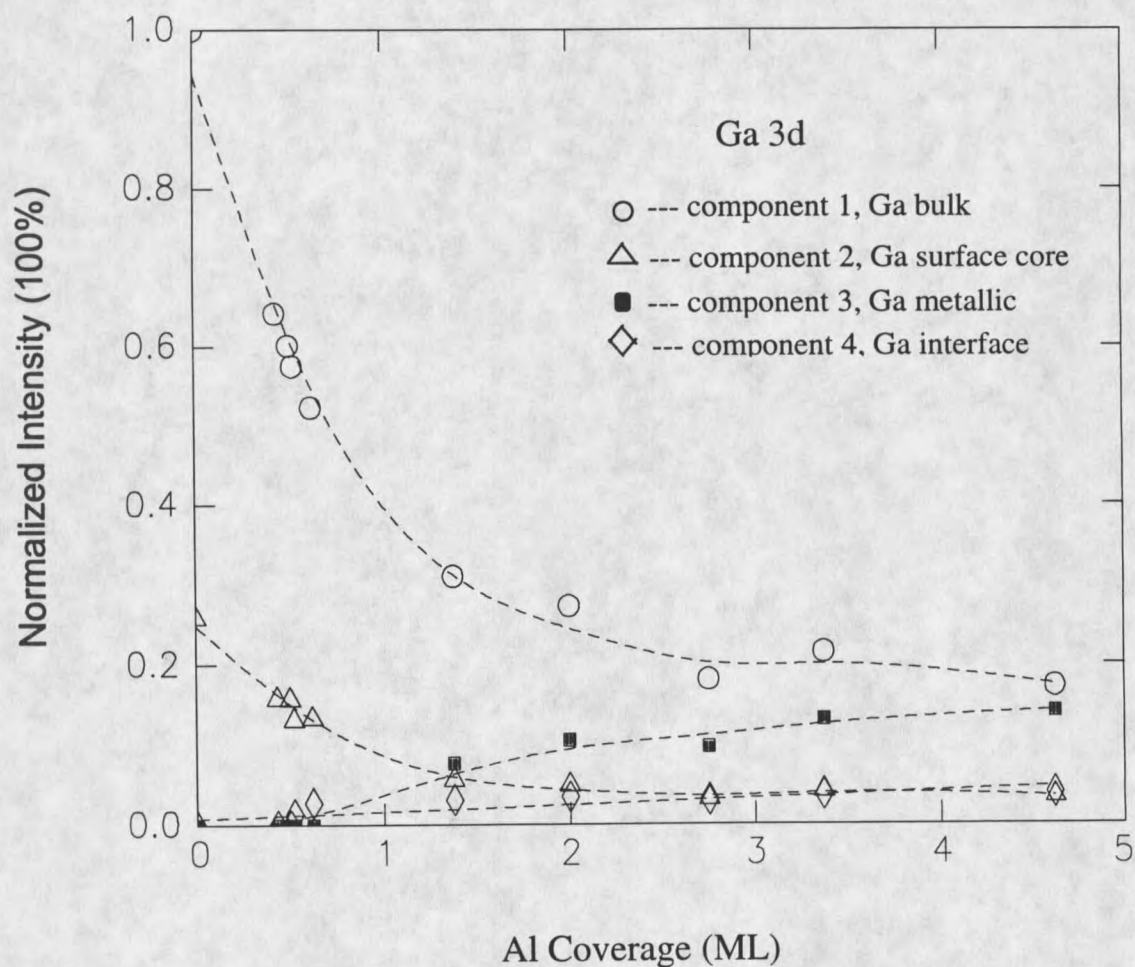


Fig. 6.7 The intensity attenuation of Ga 3d core level obtained by voigt fitting. Different components are plotted as a function of Al coverage. The intensities are normalized to the bulk Ga 3d intensity of the metal free GaN surface.

compared to the bulk Ga 3d_{5/2} at high Al coverage (> 7-8 ML). Its intensity increases with the Al coverage (Fig. 6.7).

The forth component is in between bulk Ga 3d and metallic Ga 3d, and starts to appear at Al coverage greater than 0.6 ML. The Voigt fit would give an obviously larger error if this forth component was not included.

The Al 2p core-level emission, as a function of Al coverage, is shown in Fig. 6.8 and Fig. 6.9. A two component fit at Al coverage of about 4.6 ML is also shown in the inset of Fig. 6.9. At low (≤ 1 ML) aluminum coverage, the Al 2p core level emission shows only one peak with constant peak position and increasing intensity (see Fig. 6.8). With further increase of Al coverage, above 1ML, a second component gradually shows up and becomes stronger and stronger at about 1.65 eV higher kinetic energy than that of the initial peak (see Fig. 6.9). A two component Voigt fit was used for Al coverage above 2 ML. The intensity growth of the total Al signal and each component, with intensity normalized to the total Al 2p intensity at ~4.6 ML, are shown in Fig. 6.10 as a function of equivalent Al coverage.

Discussions

The intensity attenuation of the bulk Ga 3d (component 1 in Fig. 6.7) indicates a growth morphology of Stranski-Krastanov mode.

Component 2 is the Ga 3d surface core-level shifted component. The surface nature of this component is readily seen by tuning the photon energy, as shown in Fig. 6.11. The larger surface core shift (0.82 eV) is probably due to the more ionic nature of GaN.

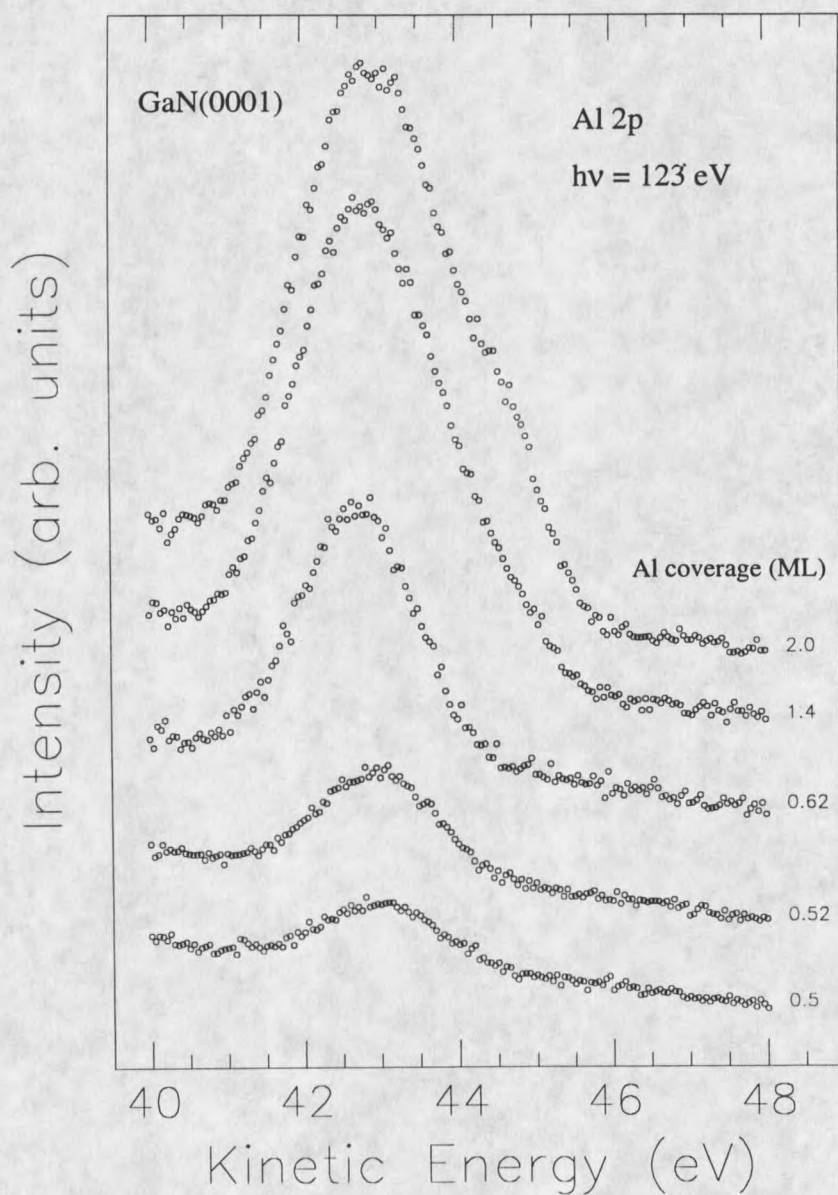


Fig. 6.8 The Al 2p core-level emission as a function of Al coverage. At low (≤ 1 ML) Al coverage, the Al core-level emission showed only one peak with constant peak position and increasing amplitude.

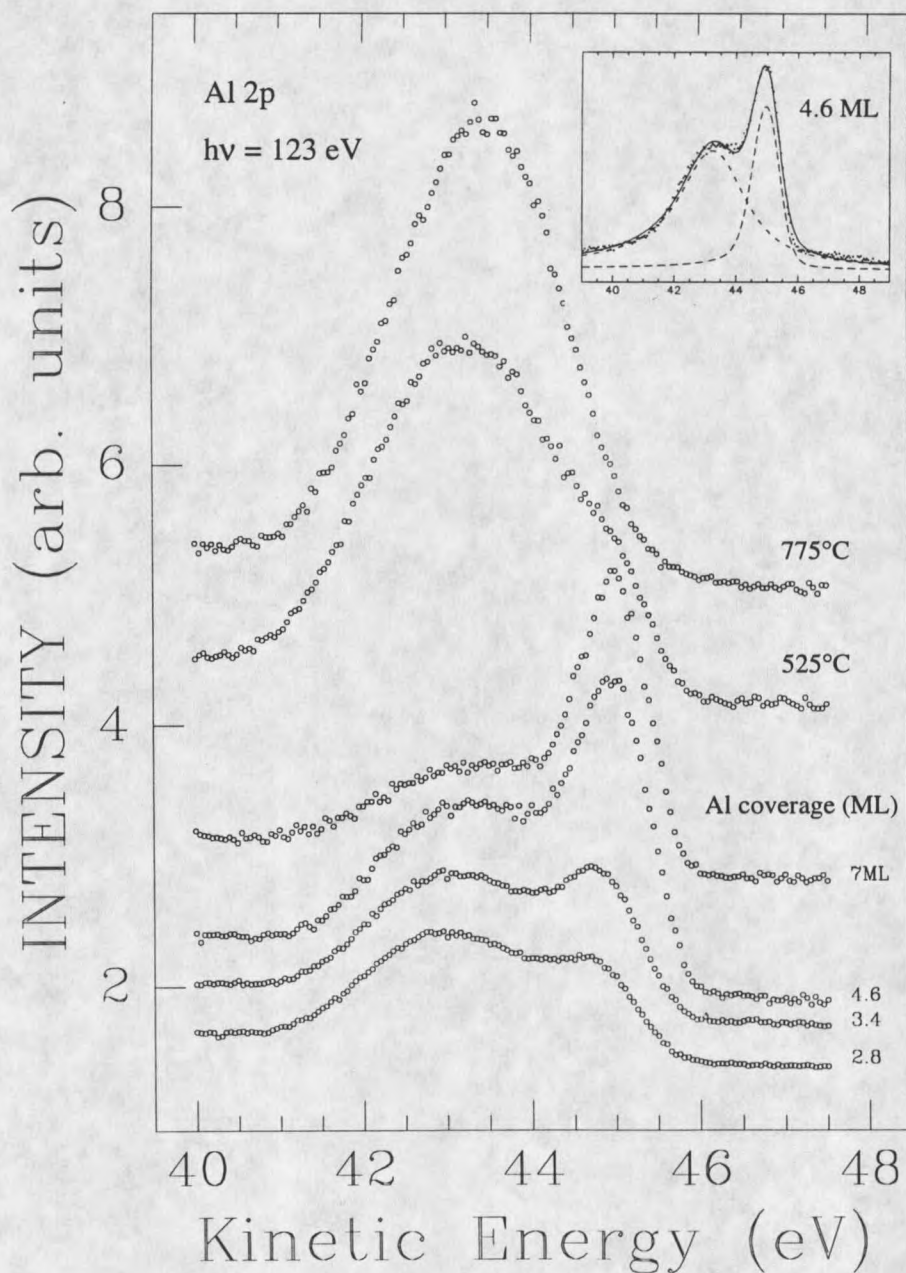


Fig. 6.9 The Al 2p core-level emission as a function of Al coverage and annealing temperature. A two component voigt fitting at Al coverage about 4.6 ML is also shown in the inset (RT).

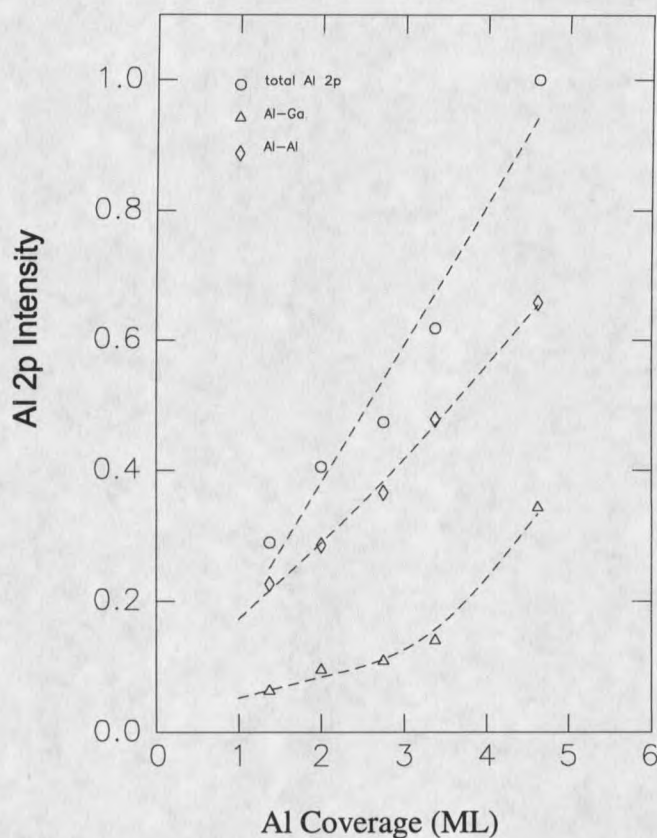


Fig. 6.10 The intensity growth of the total Al signal (circles) and each component, with intensity normalized to the total Al 2p intensity at ~ 4.6 ML, as a function of equivalent Al coverage.

D. Behr et al.¹⁰¹ found, by Raman scattering, a strong polar character of Ga-N bond, significantly more polar than the bonds in conventional III-V compounds.

Fig. 6.6 lower panel shows the Ga 3d Voigt fit with two components, and the difference spectra (solid line below) on the clean surface. One of the criteria for a good fit is that the difference spectra of the fit, minus the data, shows only random noise.¹⁰²

Note that the Ga 3d component, at 0.82 eV higher binding energy, is unlikely due to the

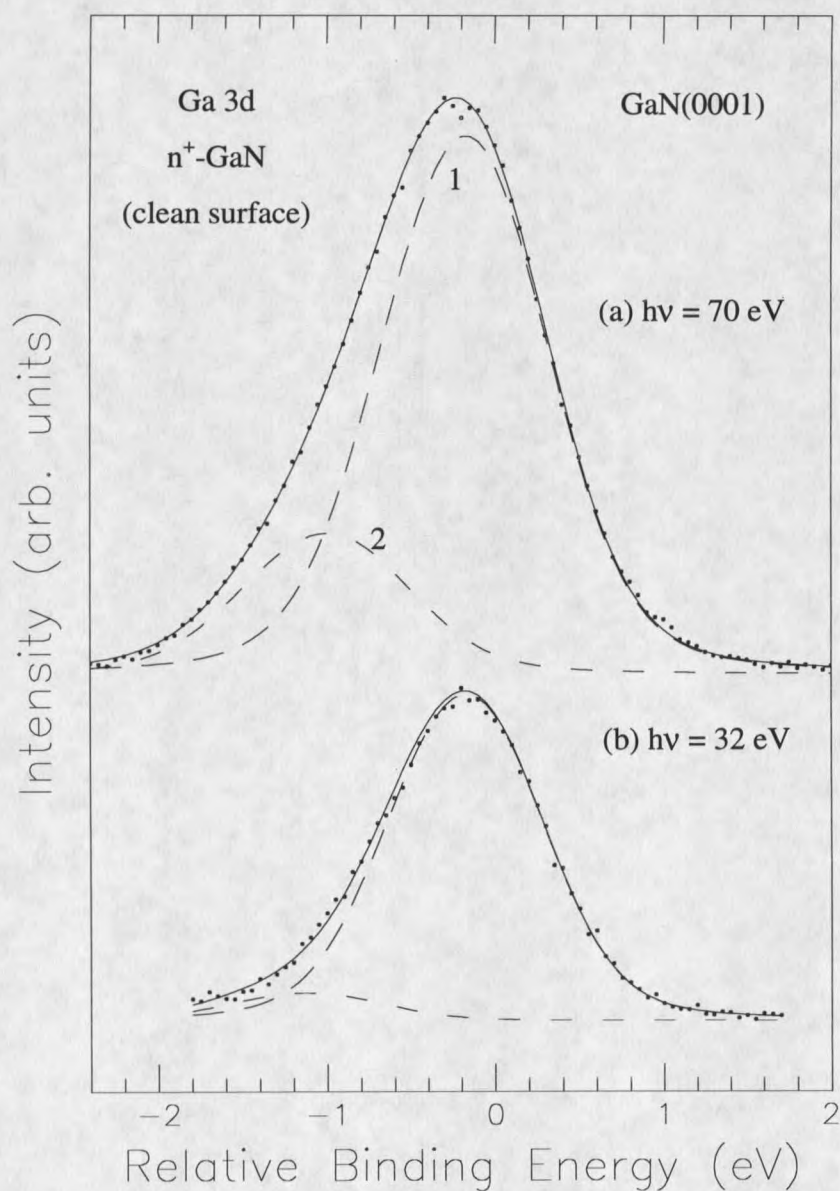


Fig. 6.11 Voigt fitting of bulk Ga 3d (component 1) and surface core-shifted Ga 3d (component 2) at (a) $h\nu = 70$ eV ($E_k \sim 45$ eV) and (b) $h\nu = 32$ eV ($E_k \sim 7$ eV).

Doniach-Šunjić asymmetry since the Doniach-Šunjić asymmetry factor has been left as a free parameter in the fitting. No good fit can be obtained with only one component.

The slow intensity attenuation rate of component 2 (Fig. 6.7) is probably due to the clustering effects as suggested by LEED studies, as well as the fact that Ga segregated to the top of the growing Al overlayer (see Fig. 6.12 below).

The deconvolution of the Ga 3d (for n^+ -GaN) core-levels yields a third component, with a shift of 1.97 eV to the lower binding energy at Al coverage of about 8 ML. We compare this to the shift of free Ga, relative to Ga-N, taken from a thick Ga overlayer deposited on GaN, as shown in Fig. 6.12. Essentially the same shift is observed in both cases from Fig. 6.12, therefore confirming the metallic nature of the third component.

Fig. 6.13 shows the third Ga 3d component (metallic Ga) shift (from the Voigt fitting) with increasing overlayer thickness; a gradually increasing shift is observed. This indicates the finite Ga bonding strength across the interface at low Al coverage.

The surface nature of the metallic Ga 3d can be readily observed by tuning the photon energy, as shown in Fig. 6.14. The kinetic energy at about 45 eV corresponds to the smallest possible electron mean free path. The higher kinetic energy (145 eV) corresponds to a mean free path well away from the minimum of the universal curve. The equivalent Al coverage is about 3.4 ML in Fig. 6.14.

The fourth component is probably due to Ga-Al bonding at the immediate interface, and some degree of Ga-Al alloying in the growing overlayer. The intensity ratio of component four to one (I_4/I_1) increases with Al coverage, indicating the occurrence of Ga outdiffusion into the top Al overlayer.

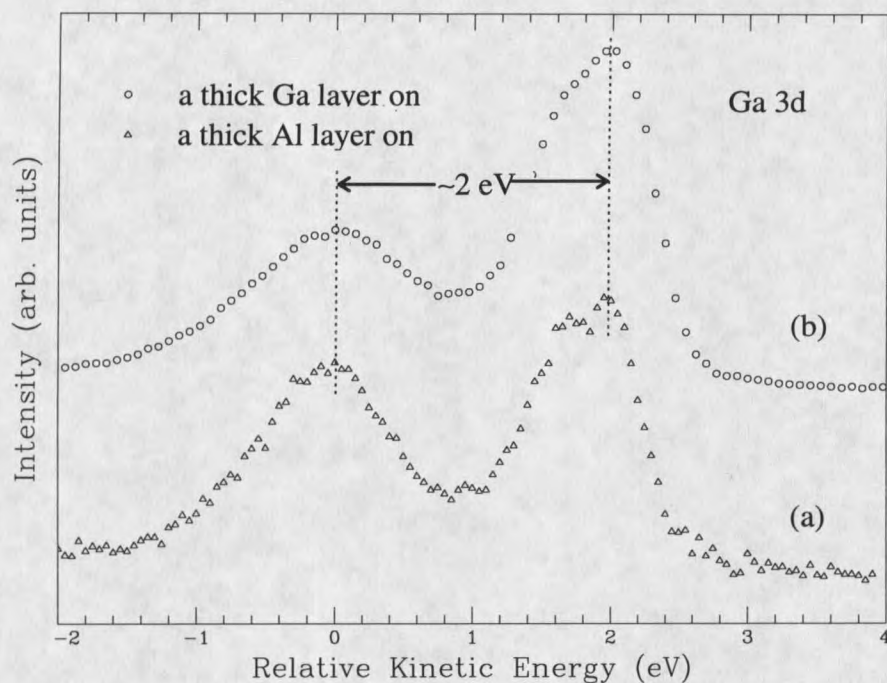


Fig. 6.12 The Ga 3d core-level spectra taken from (a) a thick Al overlayer on GaN (Al coverage about 8 ML), and (b) a thick Ga overlayer on GaN. Essentially the same shift (1.97 eV) is observed in both cases.

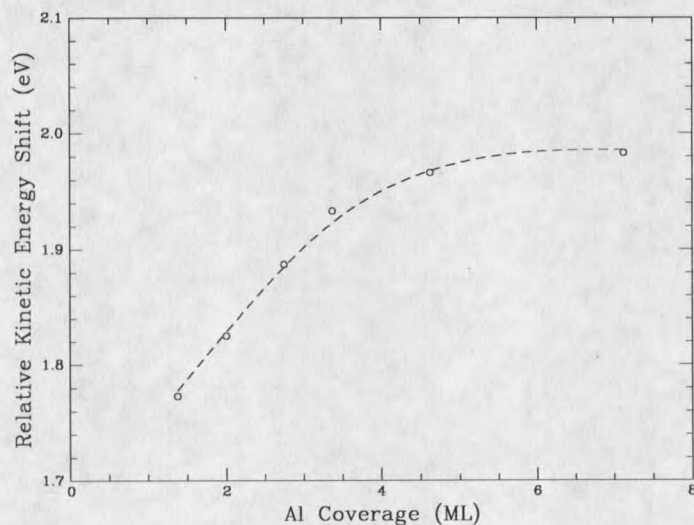


Fig. 6.13 The chemical shift from the Ga 3d third component with the increase of overlayer thickness. The gradual increase of the shift indicates the finite Ga bonding strength across the interface at low Al coverage.

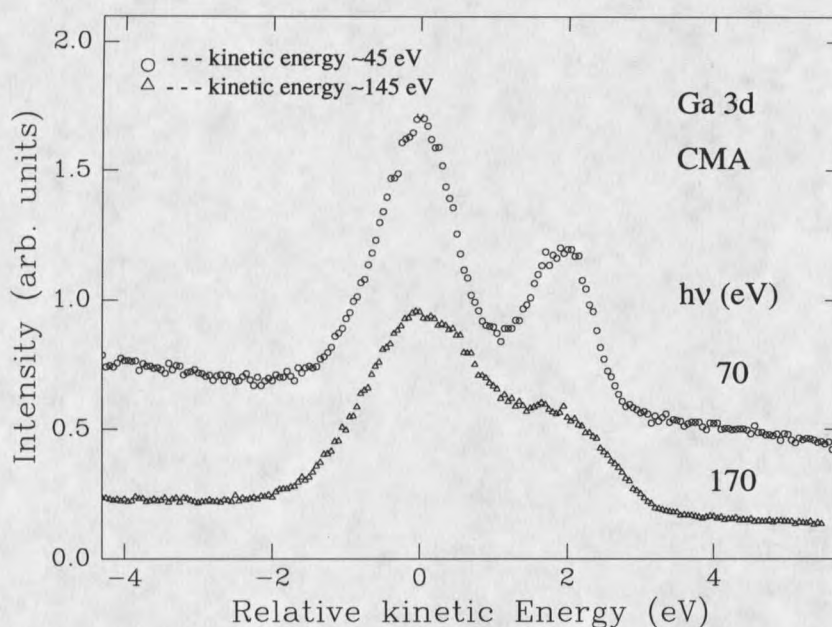


Fig. 6.14 The surface nature of the metallic Ga 3d can be readily observed by tuning photon energy, with photoelectron kinetic energy at about 45 eV for the smallest electron mean free path and away from the minimum universal curve with kinetic energy 100 eV higher.

Now we turn to the discussion of the Al 2p core-level emission shown in Fig. 6.8, 6.9 and 6.10. The overall Al signal in Fig. 6.10 increases almost linearly up to ~4.6 ML. The metallic intensity increases with Al coverage, indicating island or cluster formation. The Al-Ga interacted component at higher binding energy also increases with Al coverage, suggesting an increasing degree of Al-Ga alloying in the overlayer which is probably due to an increased Ga outdiffusion from the substrate.

The surface nature of the metallic Al 2p is also readily observed by tuning photon

energy, as shown in Fig. 6.15, with the photoelectron kinetic energy tuned at about 45 and 75 eV. The equivalent Al coverage is about 3.4 ML in Fig. 6.15.

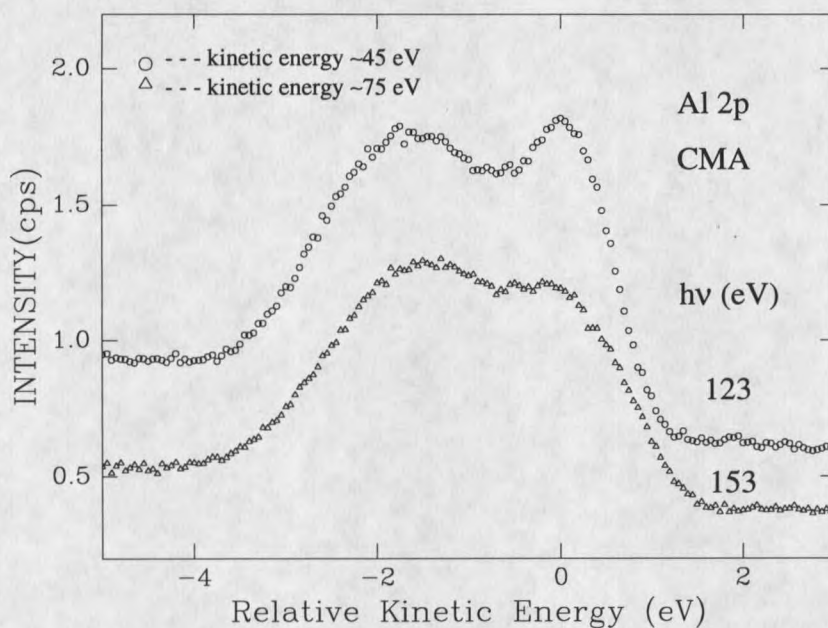


Fig. 6.15 The surface nature of the metallic Al 2p can be readily observed by tuning photon energy, with photoelectron kinetic energy at about 45 for the smallest electron mean free path and away from the minimum in the universal curve with kinetic energy several tens eV higher.

The lower binding energy Al peak due to metallic Al is substantially narrower than the high binding energy component (Fig. 6.9) and has an asymmetric factor equal to ~ 0.2 at Al coverage of 7 ML. The higher binding energy Al component is due to Al atoms chemisorbed on the surface bonding to the substrate atoms. The large width of the initial

peak might reflect the distribution of in-equivalent adjustment and reaction sites. We thus assign the initial peak being Al bonded to interface Ga and segregated overlayer Ga.

The above assignment is supported by the following facts. First, the separation between the high binding energy component and the metallic component is ~ 1.65 eV which is smaller than what would be expected if Al was bonded mainly to more electronegative species, such as nitrogen or oxygen. The Al 2p metallic peak is at 2.7 eV higher kinetic energy than that of chemically shifted Al 2p attributed to Al_2O_3 .³⁵ K. Prabhakaran¹⁰³ et al. have also reported that deposition of Al on GaN(0001) at RT gives rise to mainly two peaks at 74.9 and 77.6 eV (2.7 eV shift), which they attribute to metallic Al and a mixture of Al oxides. We thus suppose that the chemically shifted Al 2p core level, due to Al bonded to N, would give a larger shift than observed here (1.65 eV).

Brillson¹⁰⁴ et. al. showed that for Al on CdS(10 $\bar{1}$ 0), Al bonded to S resulted in a 2.4 eV chemical shift to higher binding energy than that of metallic Al 2p. Simultaneously, the Al-S bonding resulted in a second S 2p emission shifted to higher binding energy by 0.8 eV after correction for the Fermi level shift due to band bending effects. In contrast to the behavior of Al on CdS, the Al/GaN(0001) interfacial interaction is more like that of the Al/GaAs(110) interface,^{35,105,106,107} where Al 2p is chemically shifted by 0.7 eV to higher binding energy compared to metallic Al 2p, and a Ga 3d shoulder shifts to lower binding energy by 0.95 eV compared to bulk GaAs-Ga 3d at Al coverage above 0.53 Å.

Second, cluster effects. The shift of a core-level to lower binding energy with the increase of metal coverage (and hence probably larger cluster size) is typically found for a

metal deposited on an inert substrate, such as amorphous carbon, Al_2O_3 and SiO_2 . This is due to cluster size effects.¹⁰⁸ For example, Au $4f_{7/2}$ (deposited on amorphous carbon, Al_2O_3 and SiO_2) shifts to lower binding energy by about 1.4 eV at high Au coverage.¹⁰⁹ This size dependence of the core-level binding energy is due to the reduced screening with decreasing cluster size. Thus, additional energy is needed to remove an electron from a cluster with a positive charge left on it. The line width of the core-level will generally decrease with increasing cluster size. The reduced degree of cluster formation, inhomogeneity in the clusters and lifetime broadening at low coverage may all contribute to the wider line width of initial Al 2p core-level. A good understanding of these cluster effects could be achieved by correlating the core-level shifts with the actual cluster size, for example by use of an electron microscope to measure the cluster size directly, which we are unable to perform at this stage.

The Al 2p core line shape suggests an initial adsorption site where the metallic species lie close together by excluding the possibility of Al-N or Al-O bonding at the immediate interface as discussed above. This is consistent with the ISS (ion scattering spectroscopy) results of a predominantly Ga terminated GaN surface (chapter 5) and the photoelectron holographic imaging results (see chapter 5) of Al/GaN(0001) obtained at half monolayer Al coverage.

No obvious N 1s chemical shift is observed at all Al coverage at room temperature after correcting the band bending effects. The initial presence of only one Al peak and the absence of lower binding energy metallic Ga emission suggests that, at low Al coverage (≤ 1 ML), no island formation takes place and insignificant Ga diffusion to the overlayer

surface at RT occurs.

Annealing

Fig. 6. 16 shows the Voigt fit of Ga 3d upon annealing up to about 525°C and 775°C. It can be readily seen that annealing at ~775°C for 2 minutes decreases component 2 obviously. The ratio of the Ga 3d component 2 (surface core-level shifted Ga 3d) to component 1 (bulk Ga 3d) drops to about 3% upon annealing at ~775°C.

Fig. 6. 17 shows the N 1s core emission, with Voigt fits, at different Al coverage and upon annealing to ~775°C. The N 1s core-level shift due to band bending is removed by choosing the higher kinetic energy component peak as the relative kinetic energy zero reference.

Several changes occur upon annealing. First, as shown in Fig. 6. 18, the N 1s area ratio of the high to low binding energy component (Fig. 6. 17) $I_{\text{high_BE}}/I_{\text{low_BE}}$ has changed. Below 2 ML, the ratio increases only slightly, but gets obviously bigger after annealing to ~775°C. Since the electronegativity of Al (1.61) is smaller than that of Ga (1.81), we expect the N-Al bond would be at a higher binding energy than that of the N-Ga, with the N-N bond at even higher binding energy. This compares to elemental As which lies at about 0.55 eV higher binding energy than As-Ga on GaAs(100).⁹⁷ The increase of $I_{\text{high_BE}}/I_{\text{low_BE}}$ upon annealing shows evidence of AlN formation. Annealing promotes the interaction between N and Al by probably releasing some of the N from the substrate. The binding energy difference between the Al 2p and the Ga 3d core-levels

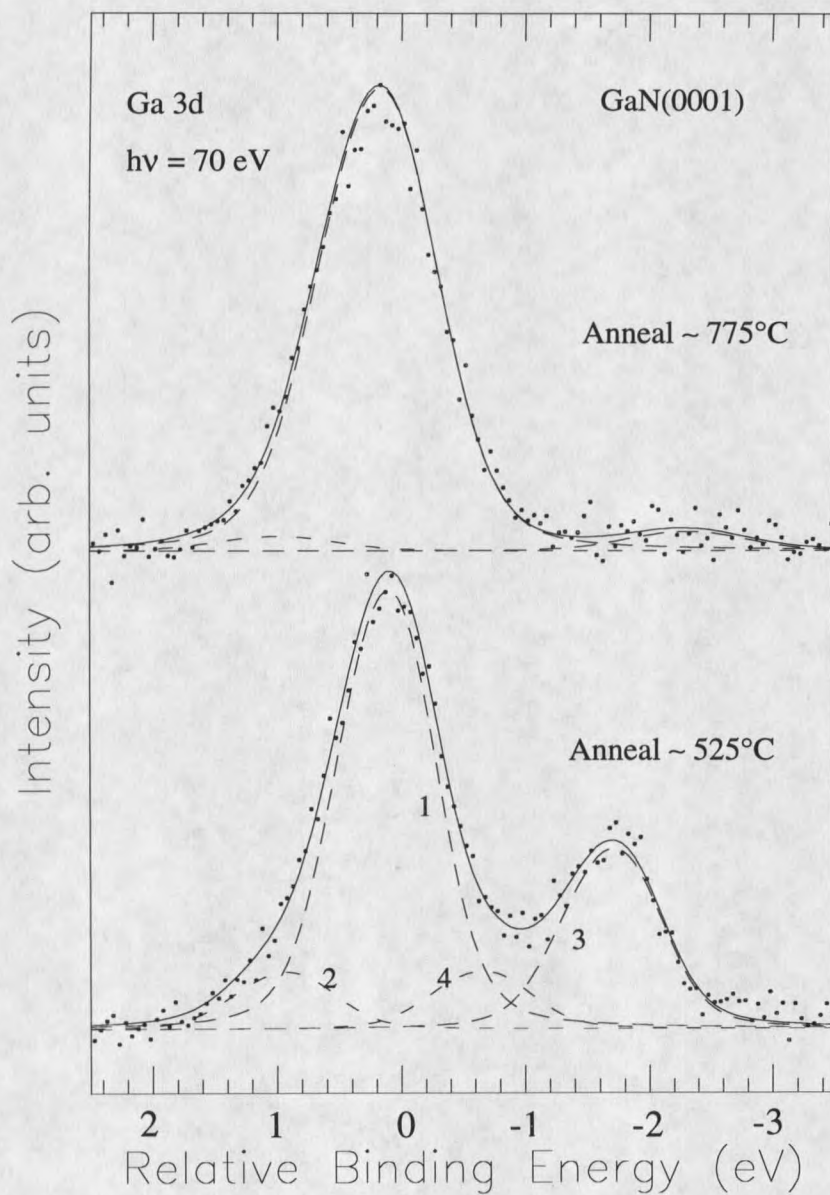


Fig. 6.16 Voigt fitting of Ga 3d upon annealing Al/GaN up to about 525°C and 775°C. Component 2 has dropped dramatically after annealing up to about 775°C.

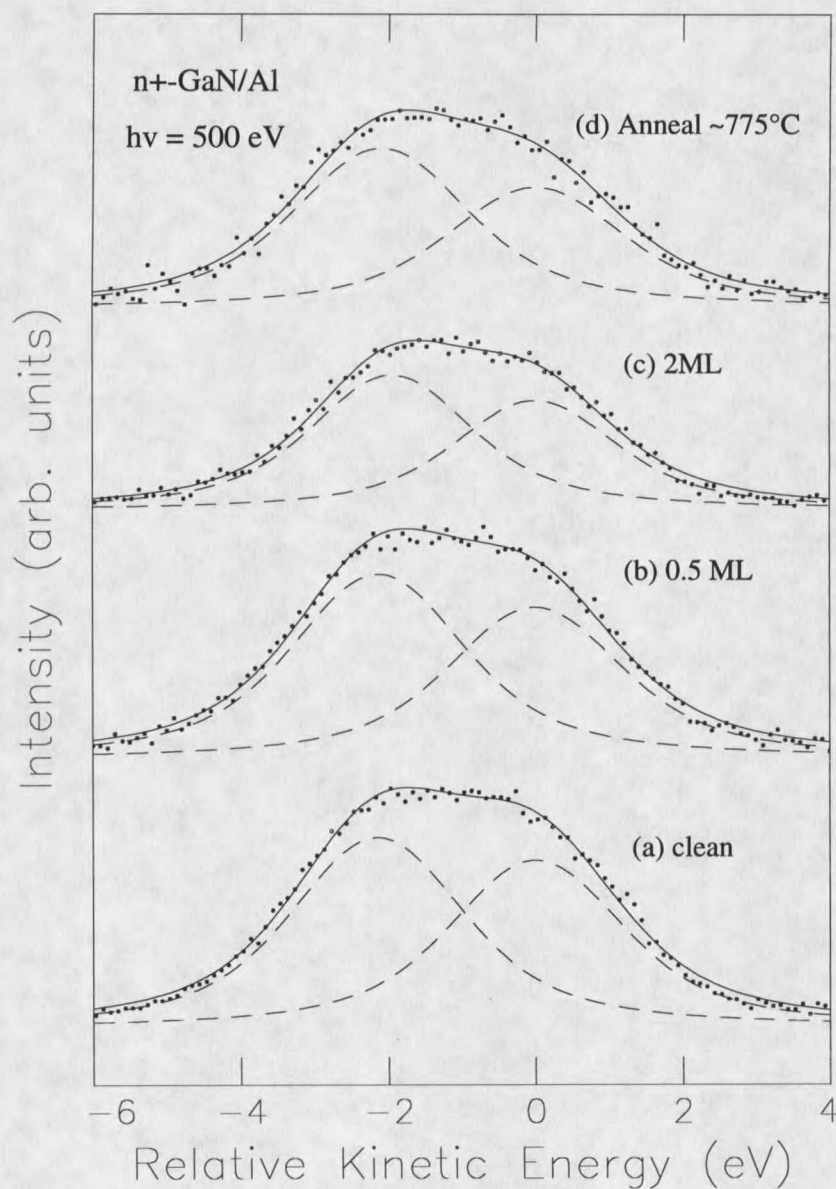


Fig. 6.17 N 1s core-level emission with Voigt fit at different Al coverage and upon annealing to $\sim 775^\circ\text{C}$. The N 1s core-level shift due to band bending is removed by choosing the higher kinetic energy component peak as the relative kinetic energy zero.

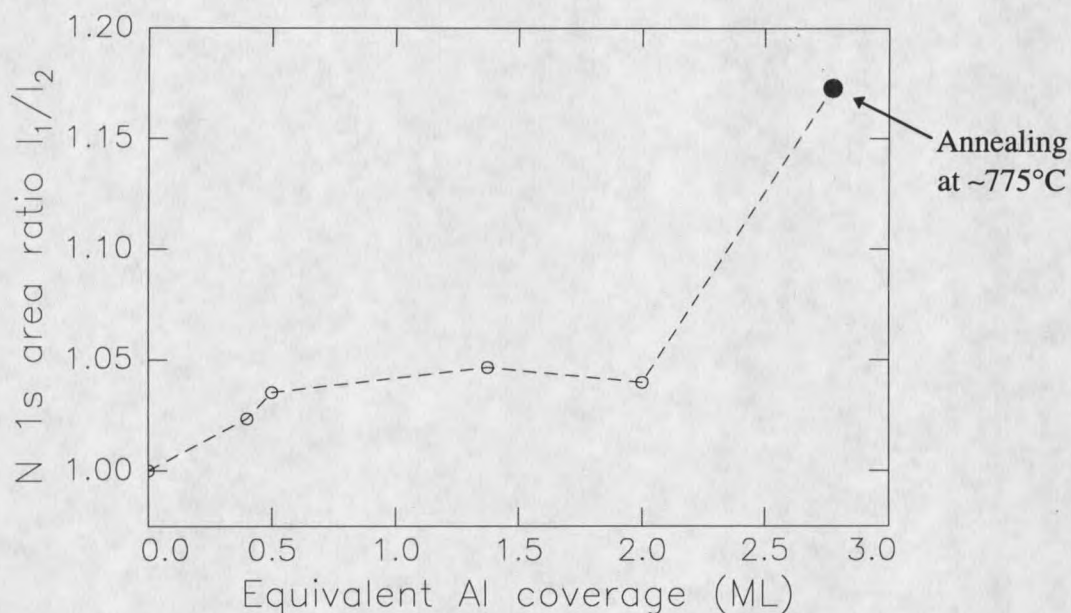


Fig. 6.18 The change of N 1s area ratio of the high to low binding energy component $I_{\text{high_BE}}/I_{\text{low_BE}}$ as a function of Al coverage.

after annealing to $\sim 775^\circ\text{C}$ is 54.5 eV, which is close to the value of 54.3 eV obtained from AlN/GaN(0001) heterojunction measurements by Martin et al.¹¹⁰ and 54.2 eV by Waldrop and Grant.¹¹¹

Second, the Gaussian width after annealing at $\sim 775^\circ\text{C}$ is slightly narrower, which indicates a more ordered overlayer. The metallic Ga and Al are totally gone upon annealing, with the metallic Ga on the surface desorbed, as in the case of annealing the Ga overlayer deposited on GaN.

Third, upon annealing to 775°C , the Al 2p peak shifts by 0.3 eV to higher binding

energy, after considering the band bending effect. This is consistent with the formation of AlN upon annealing. The increase of the Al 2p signal with increasing annealing temperature suggests that on one hand, aluminum may not diffuse into the GaN substrate, and on the other hand, annealing leads to a smoother Al overlayer (decreased island formation), and therefore a smaller average overlayer thickness gives rise to a higher Al signal. The Al 2p full width at half maximum is also larger, which may be due to the strain caused by the lattice mismatch of thin thickness AlN/GaN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ /GaN at the interface.

Fourth, both the Ga 3d and the N 1s core-level emissions shift to higher kinetic energy, indicating the change of band bending. The shift is 0.25 eV relative to the metal-free surface and corresponds to a higher Schottky barrier height (more upward band bending) of 1.2 eV (see Fig. 6. 4) before annealing and 1.45 eV after anneal ($\sim 775^\circ\text{C}$) assuming the interface dipole remains the same. The increase of Schottky barrier height might be due to the increase of the bandgap with the formation of AlN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$, as indicated by the annealing studies. In equilibrium, the Fermi level of the n^+ -type GaN will tend to move towards the VBM relative to the Fermi level of the undoped wider band gap AlN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (will be near mid gap if unpinned). The increase of Schottky barrier height upon annealing has also been observed for Al/GaAs(001) by S. A. Chambers.¹¹² Annealing the interface thus allows the study of the connection between changes in Schottky barrier height with the interfacial chemistry going on between the metal and the GaN substrate.

Schottky Barrier Height

Work function changes ($\Delta\phi_s$) are due to the combined changes in band bending (ΔqV_B) and electron affinity ($\Delta\chi$).¹¹³ The change in the band bending ΔqV_B can be obtained from the movement of the bulk Ga 3d peak position and the surface work function can be monitored by the change of vacuum level:¹¹⁴

$$\phi_s = \phi_{CMA} + K.E_{\text{threshold}} + eV_{\text{bias}} \quad (6-5)$$

The change of surface work function $\Delta\phi_s$ and band bending ΔqV_B , versus Al coverage, are shown in Fig. 6. 19. The dipole voltage $\Delta\chi = \Delta\phi_s - \Delta qV_B$ is negative (with surface more positive than layers below) at all Al coverage, with a maximum dipole voltage of -0.45 eV at about 0.53 ML, as schematically illustrated in Fig. 6. 20.

The Schottky barrier height of the interface could be altered by a dipole voltage. However, due to the small scale of interface dipole thickness, typically on the order of a few Ångstroms, it is highly probable for electrons to tunnel through this microscopic region. In this case, the dipole voltage would not contribute to the macroscopic Schottky barrier height.³⁷

As shown in Fig. 6. 20, $\phi_B = qV_B + (E_c - E_F)_{\text{bulk}} + \Delta\chi$. For $\Delta\chi = -0.45$ eV, the Schottky barrier height ϕ_B is about 0.7 eV ($1.2 - 0.05 - 0.45$) and 1.15 eV ($1.2 - 0.05$), respectively, with and without taking into account the dipole voltage contributions for Al on n^+ -GaN.

Notice that should the metal-free n^+ -type GaN have no band bending initially, the Schottky barrier height would be negligible and would show a nearly ohmic contact for

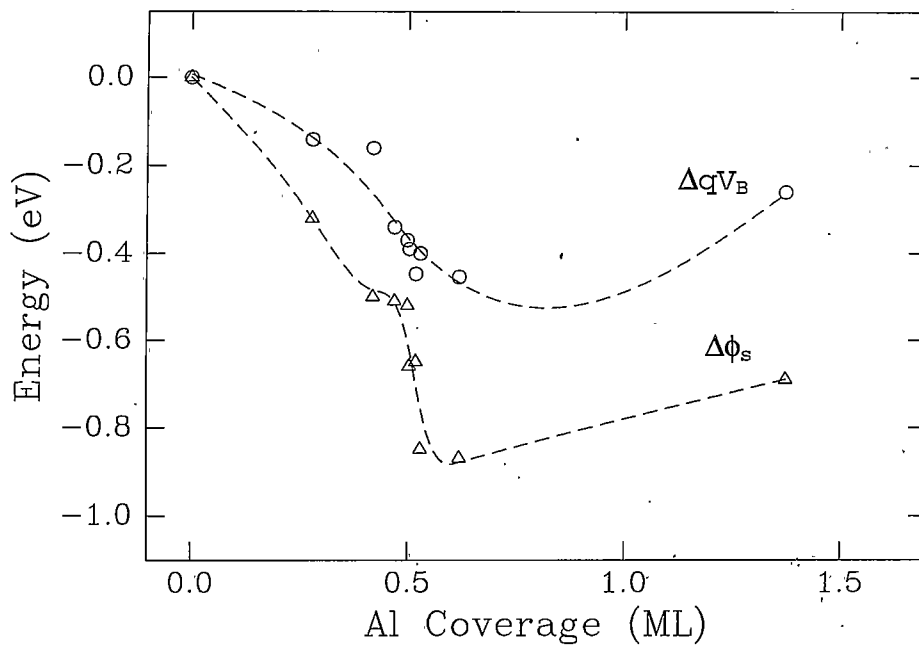


Fig. 6.19 Change of surface work function $\Delta\phi_s$ and band bending ΔqV_B on n^+ -type GaN as a function of Al coverage.

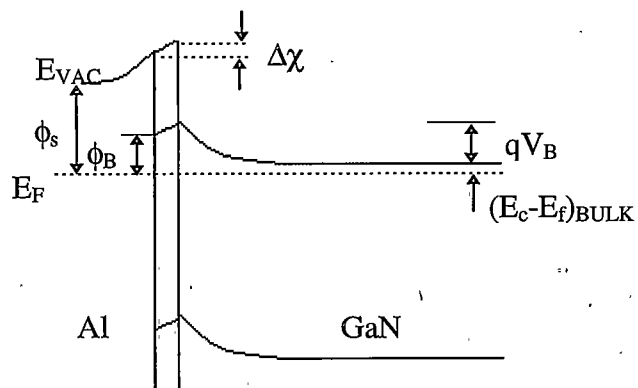


Fig. 6.20 Schematic illustration of interface dipole $\Delta\chi$, where qV_B is band bending within the surface space charge region of GaN and ϕ_s is surface work function.

Al/n⁺-GaN, as reported by B. P. Luther et al.¹¹⁵ But for Al on p-type GaN it exhibits a relatively high Schottky barrier height.

The change of the surface work function $\Delta\phi_s$ and the band bending ΔqV_B versus Al coverage for Al on p-type GaN(0001) is likewise shown in Fig. 6. 21, $\Delta\phi_s$ decreases gradually, changing to the bulk Al work function with the increase of Al coverage. The dipole voltage $\Delta\chi = \Delta\phi_s + \Delta qV_B$ is negative (also surface more positive than layers below), with the dipole voltage equal to -0.4 eV at about 0.65 ML, as schematically illustrated in Fig. 6. 22. Thus for $\Delta\chi = -0.4$ eV, the Schottky barrier height $\phi_B (qV_B + (E_F - E_v)_{\text{bulk}} + |\Delta\chi|)$ is about 3.03 eV (2.5+0.13+0.4) and 2.63 eV, respectively, with and without taking into account the dipole voltage contributions for Al on p-GaN.

Change of Local Density of States Near the Fermi Level

Fig. 6. 23 shows the upper valence band (VB) energy distribution curves (EDC) at various Al coverages, with the Fermi level as the energy reference level. The rigid shift of the valence band due to band bending has been removed by aligning the bulk Ga 3d core-level in the EDC's of Fig. 6. 23. On a clean surface (bottom EDC), and at Al coverage < 0.5 ML, there is a strong emission below the VBM of about 0.5 eV, which is the intrinsic occupied GaN surface state from the angle-resolved photoemission studies in Chapter 4. This feature gradually diminishes with increasing Al deposition. The other valence band feature does not change much with increasing Al coverage. An occupied density of states starts to develop in the gap near E_F , which indicates the conversion from semiconductor

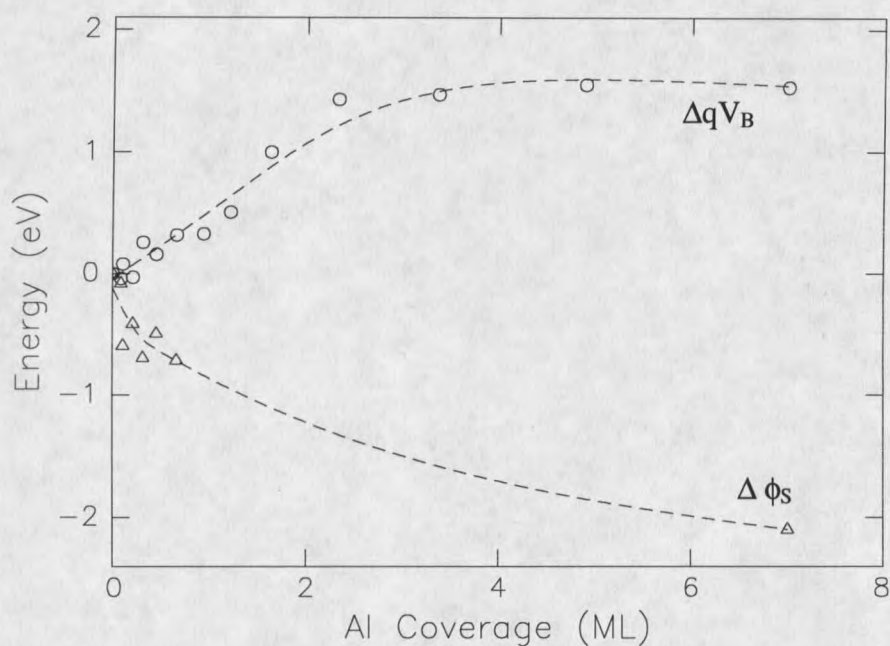


Fig. 6.21 Change of surface work function $\Delta\phi_s$ and band bending ΔqV_B for p-type GaN as a function of Al coverage.

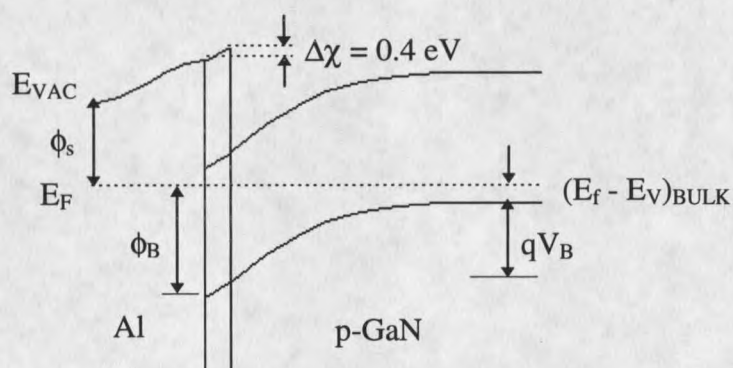


Fig. 6.22 Schematic illustration of interface dipole $\Delta\chi$ for p-GaN.

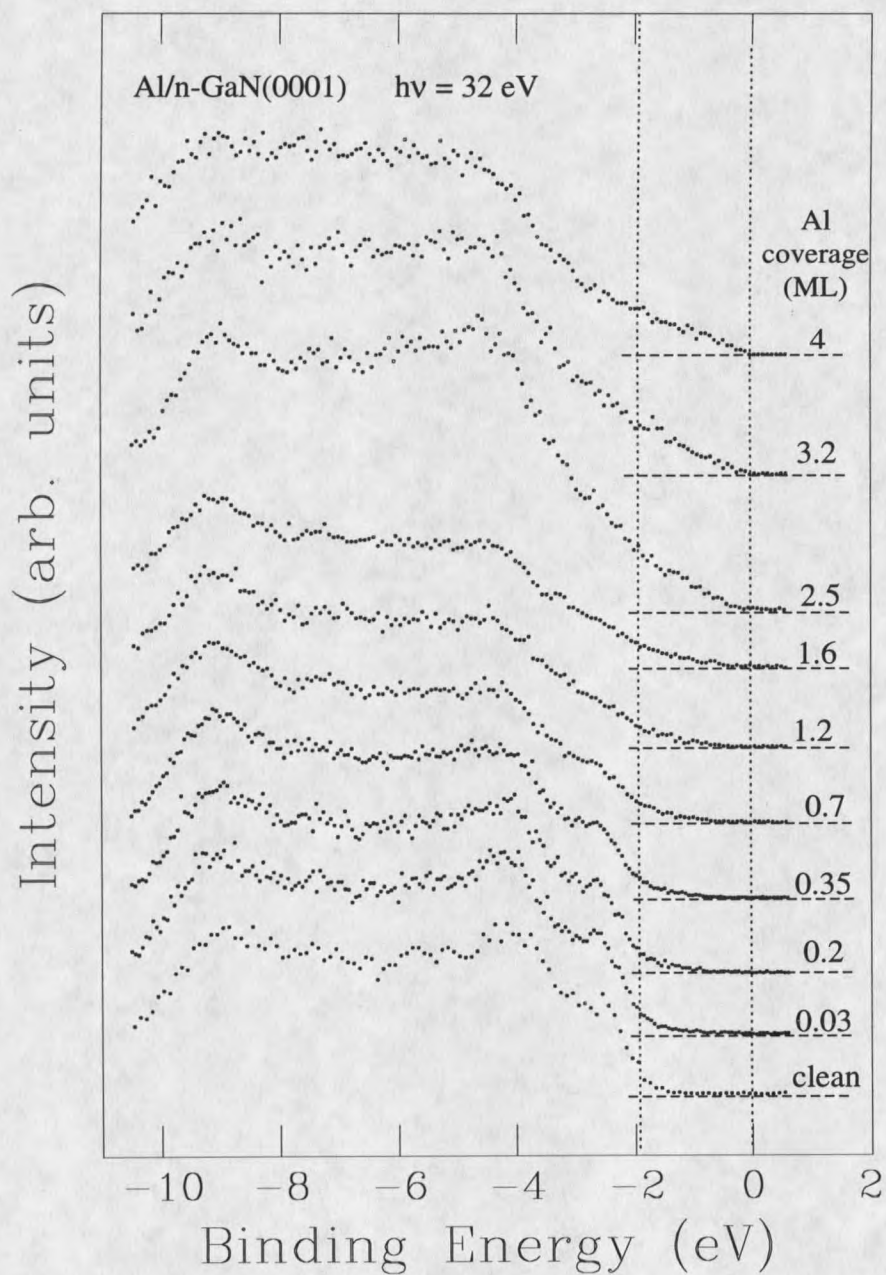


Fig. 6.23 Valence band EDC's for Al/GaN(0001) taken at $h\nu = 32$ eV as a function of Al coverage. Band bending effect has been removed by aligning the Ga 3d core level.

to semi-metallic character. This could also be due to the Al-induced gap states (MIGS-Metal Induced Gap States) calculated by Cohen for the Al/Si(111) interface.⁶⁷

Summary

A metal-semiconductor interface was formed by Al *in situ* deposition on n^+ - and p-type GaN(0001)-(1×1) at room temperature. High resolution core-level photoemission with synchrotron radiation and LEED studies have been used to determine the growth morphology and electronic structures of the Al/GaN(0001) interface and the interface upon annealing. The chemical reaction taking place at the Al sites on n^+ - and p-type GaN(0001) is followed using the photoemission spectra of the Ga 3d and Al 2p core-levels as a function of Al coverage, both at room temperature and upon annealing up to ~775°C. The formation of a Schottky barrier is followed by accounting for the line shape changes, the shifts of the bulk Ga 3d core level binding energy, the change of surface work function, and the deduced dipole voltage contribution to the Schottky barrier height. The results are summarized below.

- 1) A LEED pattern persists until an Al coverage of about 3 ML. The growth morphology is a modified Stranski-Krastanov type, i.e. only the first one half to one monolayer is two dimensional and then islands (clusters) form at higher Al coverage.
- 2) Chemical interactions at the interface lead to free Ga segregated to the overlayer surface and into the growing overlayer, with possible Al-Ga alloy formation at Al coverage above 1 ML. The initial presence of only one Al peak and the absence of

metallic Ga emission, suggests that at low Al coverage (≤ 1 ML) no island formation takes place and insignificant Ga diffusion to the overlayer surface occurs at RT. No obvious N 1s chemical shift is observed at all Al coverage at RT after correcting the band bending effects. The Al 2p core line shape suggests an initial absorption site where the metallic species lie close together. The core-level shifts of Al 2p to lower binding energy could be partly due to cluster size effects accompanying the increase of Al overlayer.

- 3) The Fermi level is pinned at about one third E_g below the CBM for both Al on n^+ - and p-type GaN(0001) which suggests donor defects at the immediate interface. These donor defects, such as N antisite or N vacancies near the interface, push E_f up towards CBM for both n- and p-type GaN.
- 4) Al/ n^+ -type GaN has a Schottky barrier height of about 1.2 eV, while Al/p-type GaN has a Schottky barrier height of about 2.6 eV, if dipole voltage contribution is not taken into account.
- 5) Upon annealing to $\sim 775^\circ\text{C}$, the N 1s line shape change indicates the formation of AlN. The Schottky barrier height on Al/ n^+ -type GaN has increased by 0.25 eV, probably due to the increase of band gap with the formation of AlN.

CHAPTER 7

METAL-SEMICONDUCTOR INTERFACES OF Sb/N⁺-GaN(0001)Results and Discussions

Changes in chemical bonding can cause charge redistribution near the interface and therefore affect the Schottky barrier height of a metal-semiconductor junction. It is thus interesting to investigate the mechanism of Schottky barrier formation by deposition of different metals on GaN(0001).

Previous work of group III metals (Al, Ga, In) on GaAs(110) ³⁷ indicates that the surface Fermi level (E_F) is pinned at the same position (about 0.8 and 0.6 eV above the VBM on n- and p-type GaAs(110), respectively), irrelevant to the metal used. The previous work of Sb (antimony) on GaAs(110) also gives the same surface E_F pinning level and is explained with the defects model. ^{116,117} The Sb/n⁺-GaN(0001) interface presents a quite different behavior from that of the Al/n⁺-GaN(0001) interface. This is related to the different interfacial chemical reaction occurring at the two interfaces.

The Ga 3d core-level energy distribution curves (EDC) taken at sequential Sb coverage are shown in Fig. 7.1. Unlike the Al/GaN(0001) interface, the Ga 3d core line shape is not changed upon deposition of Sb, indicating the absence of any chemical reaction. The bulk Ga 3d binding energies obtained from Voigt fitting are used to monitor

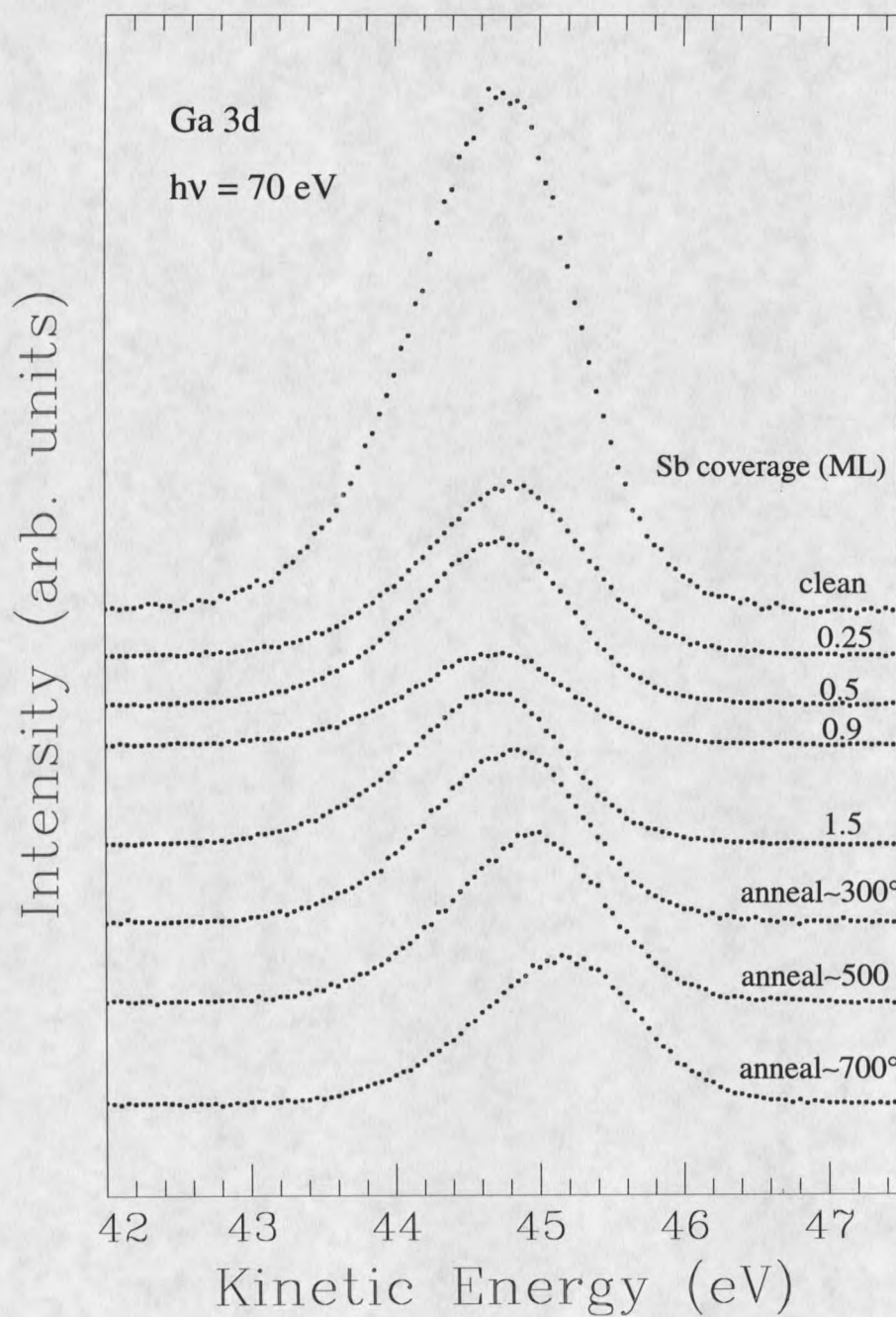


Fig. 7.1 Ga 3d core-level EDC's taken at different Sb coverage and upon annealing.

the band bending effects as a function of Sb coverage. The surface Fermi level is pinned at almost the same position as that of metal-free surface, as shown in Fig. 7.2. The slight increase (0.06 eV) of the surface Fermi level towards the conduction band minimum (CBM) could be within the experimental error. Upon annealing the overlayer (Sb thickness of about 1.5 ML), Sb desorbs readily, with about 0.4, 0.2 and 0.15 ML left after annealing up to about $\sim 300^\circ\text{C}$ for 3 minutes, $\sim 500^\circ\text{C}$ for 3 minutes and $\sim 700^\circ\text{C}$ for 2 minutes, respectively. Annealing above $\sim 800^\circ\text{C}$ desorbs the entire Sb overlayer and restores the 1×1 LEED pattern of the starting clean surface. The annealing obviously causes a more upward band bending, as shown in Fig. 7.2, and therefore gives rise to a higher Schottky barrier height.

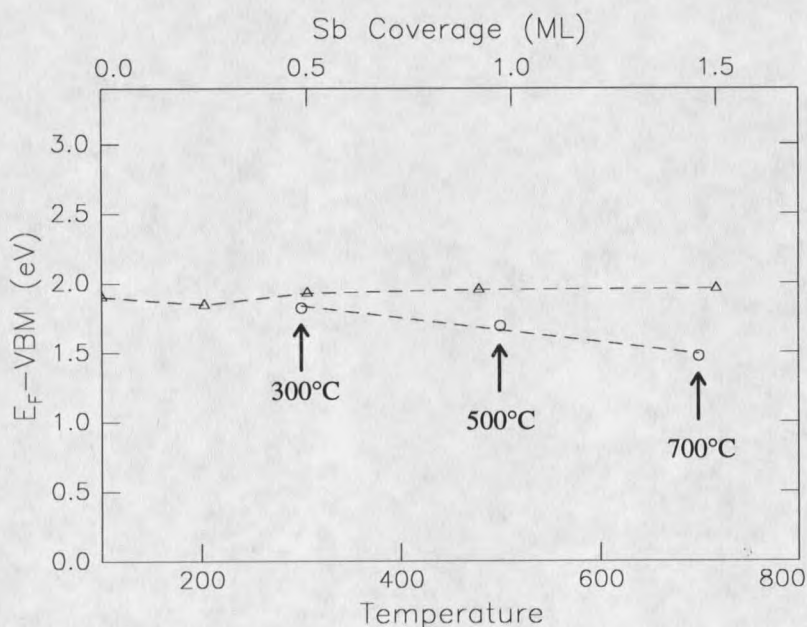


Fig. 7.2 Fermi level referenced to VBM as a function of Sb coverage (top axis) and as a function of annealing temperature (bottom axis).

The valence band structure is also recorded at sequential Sb coverages as shown in Fig. 7.3. Previous studies of Sb-semiconductor interfaces indicate that Sb can be either semiconducting α -Sb or metallic β -Sb, with semiconducting α -Sb most likely at low coverage due to strong quantum size effects.¹¹⁸ The valence band density of states near the Fermi edge, shown in Fig. 7.3, shows about the same onset below E_F and is thus most likely semiconducting at this low coverage. The inset in Fig. 7.3 shows the density of states near the Fermi edge obtained from a thick Sb overlayer (Ga 3d core-level signal has been attenuated under detection). It shows a clear Fermi edge and is indeed due to metallic β -Sb.

The difference between the surface E_F pinning on Sb/GaN from that of Al/GaN is most likely due to the different chemical reactions occurring at the interface. The absence of a Ga 3d core line-shape change on the Sb/GaN interface would reduce the N_{Ga} antisite defects caused by Ga surface segregation in the case of Al/GaN, and thus leads to an almost stabilized E_F pinning position without further introduction of the nitrogen related donor defects.

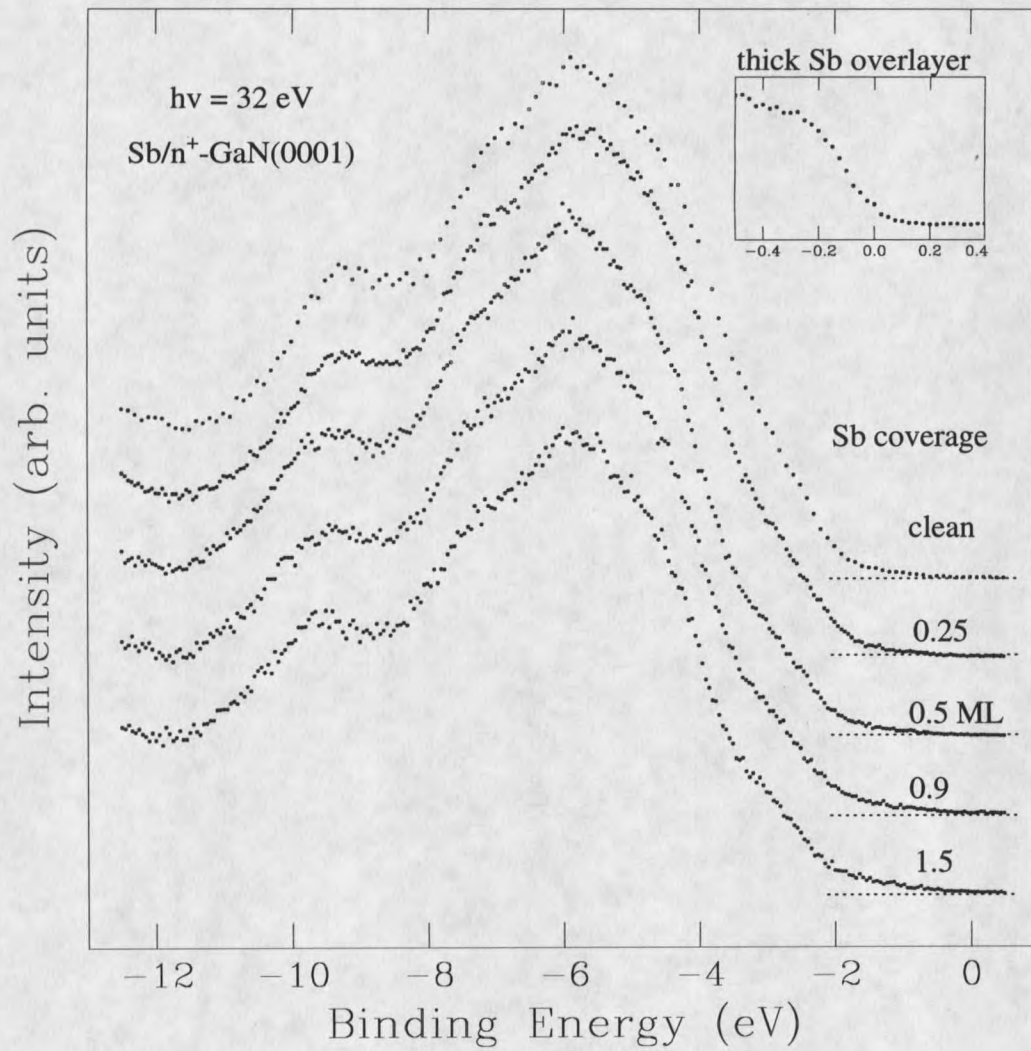


Fig. 7.3 Valence band structure taken at different Sb coverages referenced to Fermi level.

CHAPTER 8

CONCLUSIONS

Angle-resolved photoemission was employed to obtain the valence band dispersions along three major symmetry lines $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Lambda K$ of the Brillouin-zone for the wurtzite GaN structure. The results can be explained by a direct transition model, as evidenced by the dispersion of valence band features with the change of photon energy and polar angle. Valence band dispersions along the $\Gamma\Delta A$, $\Gamma\Sigma M$ and $\Gamma\Lambda K$ symmetry lines of the Brillouin-zone are obtained using the nearly free-electron final states approximation. The experimental results agree well with the calculated bands. A relatively broad N 2s peak is found to give the strongest photoemission in the photon energy range $50 \leq h\nu \leq 65$ eV. It is found to disperse very little with changing photon energy at normal emission and is located at about -14.9 eV referenced to the valence band maximum, which is about 3 eV above the Ga 3d core emission (-17.9 eV). This indicates that the hybridization of the N 2s and Ga 3d states is not as strong as predicted by the plane-wave pseudopotential method which includes Ga 3d electrons as valence electrons in the calculations and has shown the N 2s band to be both below and above the Ga 3d band. The feature near the valence band maximum does not disperse in normal emission and disperses less than 0.4 eV with the change of polar angle. Together with the Bromine contamination test, this feature is believed to be an occupied surface state.

Atomic termination of the surface is determined by ion scattering spectroscopy. The spectra clearly show a Ga-terminated surface. The local site symmetry for aluminum is determined from photon-energy-dependent photoelectron-diffraction data which are inverted by the holographic principle to obtain a real-space image. This technique is a direct experimental measurement which is model independent. The transformed Al 2p emission data yield a real space image of the Al emitter's nearest neighbor atoms. The intensity of the transform shows that the Al has two inequivalent adsorption sites. One is directly above the surface Ga, the on-top site, and the other involves replacing the surface Ga, the replacing site. The replacing site is found to be more favorable upon annealing. By selection of the Al level one knows the elemental identity of the emitter, but the data does not tell one the elemental identity of the scatterer. The ISS data indicates that the Al emitter is on top of the surface Ga atom.

A metal-semiconductor interface is formed by *in situ* Al deposition on n^+ - and p-type GaN(0001)-(1 $\times$ 1) at room temperature. The results are 1) A LEED pattern persists until an Al coverage of about 3 monolayers. The growth morphology is of a modified Stranski-Krastanov type, i.e. only the first one half to one monolayer is two dimensional and then islands (clusters) form at higher Al coverage. 2) Chemical interactions at the interface lead to free Ga segregation at the overlayer surface and into the growing overlayer, with possible Al-Ga alloy formation at Al coverage above 1 monolayer. The initial presence of only one Al peak, and the absence of metallic Ga emission, suggest that at low Al coverage (≤ 1 monolayer) no island formation takes place and insignificant Ga diffusion to the overlayer surface occurs at room temperature. The Al-2p-core line-

shape suggests an initial absorption site where the metallic species lie close together. The core-level shifts of Al 2p to lower binding energy could be partly due to cluster size effects accompanying the increase of the Al overlayer. 3) The Fermi level is pinned at about one third band-gap below the conduction band minimum for both Al on n^+ - and p-type GaN(0001) which suggests donor defects at the immediate interface. These donor defects, such as N antisite or N vacancies near the interface, push E_F up towards conduction band minimum for both n- and p-type GaN. 4) Al/ n^+ -type GaN has a Schottky barrier height of about 1.2 eV, while Al/p-type GaN has a Schottky barrier height of about 2.6 eV, if a dipole voltage contribution is not taken into account. 5) Upon annealing to $\sim 775^\circ\text{C}$, the N 1s line shape change indicates the formation of AlN. The Schottky barrier height on Al/ n^+ -type GaN increases by 0.25 eV, probably due to the increase of band gap with the formation of AlN.

Changes in chemical bonding can cause charge redistribution near the interface and therefore affect the Schottky barrier height of a metal-semiconductor junction. It is thus interesting to investigate the mechanism of Schottky barrier formation by deposition of different metals on GaN(0001). Another metal-semiconductor interface is formed by *in situ* Sb deposition on n^+ -type GaN(0001) at room temperature. The difference between the surface E_F pinning on Sb/GaN from that of Al/GaN is most likely due to the different chemical reactions occurring at the interface. The absence of a Ga 3d core line-shape change on the Sb/GaN interface would reduce the N_{Ga} antisite defects caused by Ga surface segregation in the case of Al/GaN, and thus leads to an almost stabilized Fermi level pinning position without further introduction of the nitrogen related donor defects.

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