STUDIES OF THE ADSORPTION OF C₂H₄, CO AND PH₃
ON THE (0001) SURFACE OF ZIRCONIUM

by

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Abstract

The work in this thesis includes crystallographic investigations with low-energy electron diffraction (LEED) for two surface structures designated Zr(0001)-(1x1)-C (one of lower C coverage and the other of higher C coverage), as well as investigations of the adsorption of CO and PH₃ on the (0001) surface of zirconium by using Auger electron spectroscopy (AES) and LEED.

For the lower-coverage Zr(0001)-(1x1)-C surface, the intensity-versus-energy (I(E)) curves for a set of diffracted beams were measured with a video LEED analyzer, and then compared with the results of multiple scattering calculations made for various structural models. Levels of correspondence between experimental and calculated I(E) curves were assessed with the reliability index proposed by Pendry, and surface geometries determined by the conditions for the best correspondence between experiment and calculation. The LEED intensity analysis suggests that under the lower C coverage, the C atoms in Zr(0001)-(1x1)-C appear to just occupy octahedral holes between the first and second layers of hcp zirconium; this is similar to the situation reported by Wong et al for the N adsorption structure formed on Zr(0001). The LEED-determined Zr-C bond distance is 2.30 Å, which is in reasonable agreement with the value determined by X-ray crystallography for bulk ZrC (2.34 Å). Only a very preliminary analysis could be attempted for the higher-C-coverage Zr(0001)-(1x1)-C structure; there the C atoms may occupy all tetrahedral holes.
between the first and second layers of hcp zirconium.

Some I(E) curves were measured for CO adsorption on the Zr(0001) surface; a (2x2) LEED pattern formed with the initial CO exposure while a (1x1) pattern occurs with greater exposures. A comparison was made with CO adsorption on the Ti(0001) surface, and with oxygen adsorption on Zr(0001). The PH$_3$ adsorption on Zr(0001) can give a (3x3) LEED pattern which is unstable and only measurable in a short energy range. Unlike H$_2$S adsorption on Zr(0001) surface, ordering to form the (3x3)-PH$_3$ surface is inhibited by the loss of phosphorus during heating. An attempt was made to find the optimal recipe to get a sharp (3x3)-PH$_3$ pattern; it appears that the R$_p$ value (a ratio of Auger peak heights to indicate coverage) should be between 1.3 to 1.6, and that the ordering temperature should be higher than 560°C.
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Chapter 1

Introduction
1.1 Modern Surface Science

During the past two decades, studies of solid surfaces to give information on chemical, electronic and vibrational properties have had great impact on materials science (e.g., in semiconductor analysis, heterogeneous catalysis, polymer coatings and corrosion phenomena) [1,2]. The surface or interface region plays an important role in all reactions between solid-gas, solid-liquid and solid-solid phase combinations. This had been recognized from the developments of the chemical sciences as early as the 19th century [3], however until recently the focus was on macroscopic properties of "real" or "dirty" surfaces of polycrystalline materials, which could not be well-characterized at the atomic level [4]. Modern surface science has introduced the concepts "clean and well-defined" surfaces, especially of single crystals. The latter is leading to new and fundamental insights into the physics and chemistry of surfaces, particularly when geometrical structure is taken into account. Attempts to understand surface properties, without having adequate knowledge of structure at the atomic level, have mostly been unsuccessful.

The clean surface approach requires experiments to be carried out under ultra-high vacuum conditions (<10⁻⁹ Torr). The necessity for this provision follows from the kinetic theory of gases which predicts that, for an ambient pressure of 10⁻⁶ Torr, a surface can be completely covered by an adsorbed monolayer in the order of 1 s, assuming that all colliding molecules stick to the surface. With the availability of ultra-high vacuum
(UHV) [5] facilities, many experimental techniques have been developed recently for the characterization of solid surfaces, with regard to chemical composition, geometrical and electronic structure, as well as chemical bonding and vibrational structure. Some fundamental questions that modern surface science tries to answer are [1,4]:

1. What is the composition in the surface region?
2. How are the surface atoms arranged with respect to each other?
3. What electronic energy levels are involved in surface bonding?
4. What motions do atoms have on surfaces?
5. How is energy exchanged between surfaces and impinging molecules?

Table 1.1 summarizes some important surface analytical techniques for obtaining information on chemical composition and geometrical and electronic structure.

Of the techniques listed in Table 1.1, the most commonly and conveniently used to answer questions related to structure and composition are the combination of low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). These are involved in the present work. LEED is perhaps the most established method for providing surface structural information, although techniques such as surface extended X-ray absorption fine structure (SEXAFS) and ion scattering are being currently refined to provide such information.
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<td>14 Field-Ion Microscopy</td>
<td>FIM</td>
<td>electric field</td>
<td>ion current</td>
<td>geometry</td>
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<tr>
<td>15 Scanning Tunneling Microscopy</td>
<td>STM</td>
<td>electric field</td>
<td>tunneling current</td>
<td>geometrical structure</td>
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1.2 Low Energy Electron Diffraction (LEED)

LEED has yielded a relatively large amount of structural information and at the present time it appears that it is the most convenient technique for the determination of surface structure. The potential of LEED was recognized in 1927 when the first experiment was performed by Davisson and Germer [21]. However the development of this technique to its full potential was inhibited by many theoretical and experimental difficulties, and it was only during the 1970's that these problems were overcome sufficiently for some surface structures to be determined [22]. The LEED experiment involves directing a monoenergetic beam of electrons, in the energy range of 10 to 300 eV, at one face of a single crystal. Roughly 1% to 5% of the incoming electrons are elastically scattered, and these electrons are collected on a fluorescent screen to give a diffraction pattern if the crystal surface is well-ordered. This pattern can consist of bright, well-defined spots; the sharpness and overall intensity of the spots is related to the degree of order on the surface. The experimental details will be presented in Chapter 2.

1.2.1 Electron Scattering

For an electron beam of energy, $E_p$, incident on a surface, there will occur both elastic backscattering and secondary electron emission. A typical energy distribution is shown in Figure 1.1. For the purpose of LEED, this distribution may be divided into three regions. Region I
Figure 1.1 Schematic indication of the energy distribution of secondary electron for an incident energy $E_p$.

Figure 1.2 Typical dependence of electron mean free path in a metallic solid as a function of energy.
contains elastically scattered electrons as well as the "quasi-elastic" electrons which have suffered small energy losses (<0.1 eV) due to interactions with surface phonons; the latter can be measured with high-resolution electron energy loss spectroscopy (HREELS). In region II, small peaks observed on the slowly-varying background correspond to inelastically scattered electrons associated with interband and plasmon excitations; in addition peaks resulting from the emission of Auger electrons are present (Section 1.3). The Auger peak energies are independent of $E_p$, and therefore they can be distinguished from the loss peaks by varying the incident energy. The so-called "true secondary electrons" emitted in region III at low energies are associated with a series of inelastic collisions between incident electrons and electrons bound in the solid. In each collision process energy can be transferred between electrons with the result that a single energetic primary electron can create a cascade of secondaries that contribute to the broad peak [6].

The wave nature of electrons ensures that the energy ($E$ in eV) is related to wavelength ($\lambda$ in Å) according to de Broglie's relation:

$$\lambda = \sqrt{\frac{150.4}{E}}$$  \hspace{1cm} (1.1)

For the energy range of LEED the electron wavelength is therefore of the same order as interatomic distances in a solid. As a result, diffraction can occur and thus elastically scattered electrons can be used to provide information about the periodic surface structure.
High surface sensitivity for the energy of LEED depends on the short mean free path $L$ (i.e., the mean distance travelled by an electron before it is scattered inelastically in the solid). Low-energy electrons experience strong inelastic scattering in solids. If the incident electron intensity is $I_0$, after travelling a distance $l$ in the solid it will be attenuated to $I$. The relationship between $L$, $I_0$, and $I$ can be expressed in terms of

$$I = I_0 \exp\left[-l/L\right]$$

(1.2)

The general form of the dependence of the mean free path length on electron energy is shown in Figure 1.2. Electrons in the low-energy range are associated with values of $L$ of just a few Å, and therefore they are ideally suited for investigation of the top few layers of a solid.

1.2.2 LEED Crystallography

The objective of LEED crystallography is to determine the positions of all atoms between the vacuum interface and the plane in the solid at which the substrate (i.e., the bulk) structure is established. A surface of a single crystal can be conveniently classified by reference to the Miller indices [9] of the parallel planes within the bulk crystal. All equivalent points in the surface region can be related by translational vectors.
\[ t = m \mathbf{a}_1 + n \mathbf{a}_2 \quad (m,n \text{ integers}) \quad (1.3) \]

Here the unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) define a unit mesh and, with the complete set of values of \( m \) and \( n \), one can generate a net in analogy with the term "lattice" in triperiodic crystallography. Five types of unit meshes analogous to the 14 Bravais unit cells of triperiodic crystallography are possible, and these are shown in Figure 1.3(a). Details of various conventions in surface crystallography can be found in an article by Wood [23].

Instead of using the unit vectors in real space, it is more convenient for representing diffraction conditions to use the corresponding vectors in reciprocal space. The real space basis vectors \((\mathbf{a}_1, \mathbf{a}_2)\) are related to the reciprocal space basis vectors \((\mathbf{a}_1^*, \mathbf{a}_2^*)\) by the following dot products:

\[ \mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi \delta_{ij} \quad (i, j = 1, 2) \quad (1.4) \]

where \( \delta_{ij} \) is the Kronecker symbol which has the values \( \delta = 1 \) or 0 for \( i=j \) or \( i \neq j \) respectively (i.e., \( \mathbf{a}_1 \perp \mathbf{a}_2^* \), and \( \mathbf{a}_1^* \perp \mathbf{a}_2 \)). The unit vectors \( \mathbf{a}_1^* \) and \( \mathbf{a}_2^* \) define a reciprocal net from

\[ g = h \mathbf{a}_1^* + k \mathbf{a}_2^* \quad (h, k = \text{integers}) \quad (1.5) \]
Figure 1.3 The five types of two-dimensional surface meshes
(a) in real space
(b) in reciprocal space.
Figure 1.3 shows the relationship between the reciprocal and real space vectors and their meshes respectively.

Consider a mono-energetic, collimated electron beam incident on a perfectly clean well-ordered surface with particular direction \((\theta, \phi)\), as is shown in Figure 1.4. There will be a small portion of the incident electron flux that is elastically back-scattered. In field free space, the incident and elastically-scattered diffracted beams can be represented by plane waves

\[
\psi_k(\mathbf{r}) = \exp(ik \cdot \mathbf{r}),
\]

where \(k\) is a wave vector which specifies the beam direction; the magnitude of \(k\) (i.e., \(2\pi/\lambda\)) relates to energy. The \(\mathbf{r}\) is the position vector in space with respect to a reference origin. For incident and diffracted wave vectors, \(k_0\) and \(k'\) respectively, the differential scattering cross-section [24] can be expressed as

\[
\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\hbar^2}\right)^2 |\langle k' | T | k_0 \rangle|^2
\]

where \(T\) is the appropriate transition operator, \(\hbar\) is Planck's constant divided by \(2\pi\), \(m\) is the electron mass, \(k_0\) is the incident wave vector and \(k'\) is the diffracted beam wave vector.
Figure 1.4 Angle conventions for incidence of an electron beam on a surface. $\theta$ is the polar angle relative to the surface normal; $\phi$ is an azimuthal angle relative to a major crystallographic axis in the surface plane.
For a symmetry operation \( S \), the matrix elements in equation (1.7) satisfy

\[
\langle \psi_{k'}, |T| \psi_{k} \rangle = \langle \psi_{k'}, |S^{-1}TS| \psi_{k} \rangle = \langle S\psi_{k'}, |T| \psi_{k} \rangle.
\]  

(1.8)

When \( S \) represents translation by a net vector \( t \),

\[
S\psi_{k}(r) = \psi_{k}(r+t) = \exp(ik\cdot(r+t)),
\]  

(1.9)

and the two ends of equation (1.8) give

\[
\langle \psi_{k}, |T| \psi_{k} \rangle = \exp[i(k_0-k')\cdot t]\langle \psi_{k}, |T| \psi_{k} \rangle.
\]  

(1.10)

This can be satisfied only if either \( \langle \psi_{k}, |T| \psi_{k} \rangle = 0 \) or \( \exp[i(k_0-k')\cdot t] = 1 \). The first corresponds to zero scattered intensity, but the second necessarily holds when \( (k_0-k')\cdot t = 2\pi n \) for \( n \) integral. This is ensured when the parallel components of the wave vectors satisfy

\[
k'_0 = k_0 + g(h,k) \quad (h, k = \text{integers})
\]  

(1.11)

where \( g(h, k) \) is the reciprocal vector defined in equation (1.5). Equation
(1.11) is a statement of momentum conservation parallel to the surface. This equation along with the conservation of energy for elastic scattering, namely

\[ |k'|^2 = |k_0|^2 \]  

(1.12)

defines the diffraction conditions for LEED. The indices \((h,k)\) in equation (1.5) can be conveniently used to label the diffracted beams (e.g. the \((0,0), (1,0), (1,1)\) beams). Figure 1.5 shows how the direction of a diffracted beam (wave vector \(k'\)) depends on the value of \(g(h,k)\) and \(E\).

From equation (1.11), the \((0,0)\) (or specular) beam is formed by electrons which have interacted with the surface without transfer of momentum parallel to the surface; therefore the position of its diffraction spot on the screen remains invariant when the incident energy is changed (provided that the electrons are moving in a field-free region and the incident beam direction is fixed). But for the non-specular beams, when \(E\) is increased, the perpendicular component of each diffracted beam (i.e., \(k'\)) is increased. This results in non-specular diffraction spots moving toward the \((0,0)\) beam on the screen.

The LEED pattern observed on a screen is due to electron diffraction occurring in the three dimensional region probed by the electrons studied. However, the pattern itself only gives information on the diperiodicity in this region; that is it gives information only about the size and shape of the unit mesh for the region probed. The LEED pattern is the reciprocal
Figure 1.5 Schematic diagram showing how the conservation conditions determine a diffracted beam's direction. The (0,0) beam results from specular reflection.
map of the surface periodicities, and cannot by itself detail atomic positions within the surface region. This extra information is obtained in LEED crystallography by analyzing the intensity of diffracted beams as a function of energy. The so-called intensity-versus-energy (I(E)) curves for various surface structures are calculated for all diffracted beams and then compared with the experimental I(E) curves to determine the correct structural arrangement. In this way such surface structural information as adsorption sites, bond lengths and interlayer spacings can be obtained.

1.2.3 LEED Pattern Notation and Domains

Adsorption often gives larger unit meshes than the clean surface; this results in extra LEED spots which are frequently called "fractional order" spots. There are two nomenclatures in use to describe the associated surface structures, namely Wood's notation [23] and matrix notation [27,28]. They both relate the unit vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) for the surface structure to those of the substrate, \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). If there is a common rotation angle, \( \theta \), between them, then Wood's notation specifies the adsorption structure as \((p\,q)\,-\theta\), where \( \frac{|\mathbf{b}_1|}{|\mathbf{a}_1|} = p \), \( \frac{|\mathbf{b}_2|}{|\mathbf{a}_2|} = q \). Reference to the angle is conventionally dropped if it is zero. For more complex surfaces the relationship between the two sets of unit vectors requires a matrix notation i.e.,

\[
\begin{bmatrix}
\mathbf{b}_1 \\
\mathbf{b}_2
\end{bmatrix}
= \begin{bmatrix}
\mathbf{a}_{11} & \mathbf{a}_{12} \\
\mathbf{a}_{21} & \mathbf{a}_{22}
\end{bmatrix}
\begin{bmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2
\end{bmatrix}
\]  

(1.13)
or \( b = A \cdot a \). The matrix \( A \) provides a general designation of a surface with respect to the substrate. Estrup and McRae have detailed the relationship in reciprocal space, that is between the LEED pattern of the substrate and that for the surface structure designated by \( A \). Figure 1.6 shows some examples of these notations which occur for adsorption on the Zr(0001) surface, as discussed in this work.

Bulk zirconium has the hexagonal close packed (hcp) structure, and the individual close packed layers, parallel to the (0001) plane, are stacked in the ABAB\(***\) sequence. When the zirconium crystal is truncated parallel to the (0001) plane, the terminations are either as ABAB\(***\) or as BABAB\(***\). In general both A terminated domains and B terminated domains occur at the surface. Further, if the two types of domain have equal probabilities of being probed by the incident electrons (Figure 1.7(a)), then LEED would give a "domain averaged" pattern which will show 6-fold symmetry at normal incidence (Figure 1.7(b)).

1.2.4 Calculation of LEED Intensities

Due to the very strong interaction between low-energy electrons and solids, the single-scattering theory used in X-ray crystallography is not suitable for LEED. In comparison to X-rays a much larger fraction of electrons are backscattered; also there is a much greater probability that the backscattered electrons will scatter elastically several times before emerging from the surface. This gives rise to structure in measured I(E) curves which is not understandable with the single-scattering (or kinematical) theory. Multiple scattering (or dynamical) calculations are,
Figure 1.6 Two unit meshes and their associated notations observed for adsorption on the Zr(0001) surface.  
(a) For adsorption of C on Zr(0001) surface.  
(b) For adsorption of O on Zr(0001) surface.
Figure 1.7 Termination at hcp(0001) surfaces:
(a) Side view with A termination and B termination.
(b) Superposition of two 3-fold symmetrical LEED patterns to form a 6-fold symmetrical LEED pattern for normal incidence.
therefore, required for LEED intensity analyses. Detailed descriptions of the theoretical methods for these multiple scattering calculations are given by Van Hove and Tong [29] and by Pendry [30,31]; the main computing programs used in this work were provided by Van Hove [32].

It has already been indicated that incident electrons in LEED experience strong inelastic scatterings in the solid; clearly the crystal potential must be chosen carefully to accommodate these two important features in LEED intensity calculations. The muffin-tin model is generally used to approximate the potential for a solid surface. In this model the potential within each atomic region is treated as spherically symmetrical. Within the interatomic region the potential is taken to be constant ($V_0$) with both real and imaginary components as in

$$V_0 = V_{0r} + iV_{0i}.$$  \hspace{1cm} (1.14)

The real component ($V_{0r}$) accounts for the lowering in potential energy which an electron experiences on entering the solid (it is sometimes loosely referred to as the inner potential); its typical value is between -5 and -15 eV. This parameter is generally set empirically and used for aligning the experimental $I(E)$ curves with corresponding calculated curves [29]. The imaginary component ($V_{0i}$) accounts for the electron damping effect due to the inelastic scattering experienced by the LEED electrons inside the solid. $V_{0i}$ is necessarily a negative quantity; it is often treated as a constant, although sometimes it is given a weak energy dependence (e.g. as $E^{1/3}$ [29]).
A number of methods are available for LEED calculations [9]. In the specific work here for the analyses of carbon on the Zr(0001) surface (Chapter 3), the layer doubling, renormalized forward scattering and combined space methods were used. They are now outlined very briefly.

A. Layer Doubling Method [29,30]

This method requires that inelastic scattering is sufficiently strong so that the scattering by a semi-infinite crystal can be approximated by the scattering from a slab of finite thickness. Two layers are considered first, then four layers, and at each level of iteration the number of layers is doubled. This stacking process is continued in the series 2, 4, 8, 16... layers until the reflection amplitudes have converged; typically this required 8 or 16 atomic layers.

The layer doubling method is efficient and flexible for varying the details of surface structures, but it requires all interlayer spacings to be greater than about 0.5 Å, otherwise there can be convergence problems. This method is particularly convenient for bulk structures having a ABAB... type of stacking sequence (e.g., Zr).

B. Renormalized Forward Scattering (RFS) Method [31]

The backward scattering off any atomic layer is usually weak compared with the forward scattering. This allows the former to be treated as a perturbation while the latter scatterings are treated exactly. The first-order calculation then includes all scattering paths with a single
backward scattering process; correspondingly the second and third order calculations have three and five back reflection processes respectively. The calculation is continued until the sum of the amplitudes of the forward scattered beams at the deepest level considered is less than some predetermined fraction of the incident beam amplitude on the first layer (e.g. 0.3%). Typically, the RFS method uses 12 to 15 layers. In this work a more recently revised subroutine RFSG was used to handle a variety of stacking sequences [32]. The RFS method provides the most efficient computation scheme for interlayer multiple scattering when all interlayer spacings are larger than about 1.0 A. For both the RFS and layer doubling methods important savings in computer requirements can be made by utilizing symmetry [29]. Where beams are equivalent they can be grouped together to effect a reduction in matrix dimension and also save computing time.

C. Combined Space Method [29,33]

The scattering problem in LEED amounts to calculating electron wave functions inside the solid which match at the interface to the wave functions outside the solid. The muffin-tin model suggests that appropriate basis functions inside the solid are provided by either plane waves (which provide the so-called K-space representation) or spherical waves (which provide the L-space representation). The layer doubling and RFS methods are K-space methods, but when small interlayer spacings occur, the number of beams that has to be included gets larger, with consequent increase in the dimension of all matrices involved in the scattering problem. This can be overcome by using L-space methods, which then become
more efficient. Indeed, the combined space method optimizes the use of both K-space and L-space representations. Specifically, it permits the rapid K-space method to be used within the main part of the crystal, where the interlayer spacings are sufficiently large, whilst the more cumbersome L-space method can be employed to treat the smaller interlayer spacings which may result for example from the adsorption of small atoms like C on to a transition metal surface.

1.2.5 Evaluation of Intensities

The determination of surface structure involves a trial and error analysis designed to find that geometrical model which gives the best match between the calculated and experimental I(E) curves. The comparisons between experiment and calculation may be done visually or mathematically. The later technique uses one or more reliability indices (or R-factors to use the terminology of X-ray crystallography) to identify the best model in the calculations. More than 10 different R-factors have been developed for LEED [34], but those introduced by Zanazzi and Jona [35] and by Pendry [36] have been particularly popular. The former is sensitive to peak shapes and height, while the latter just emphasizes the positions of peaks and troughs; both have the same feature that the smaller the R-factor, the better is the match up between the sets of experimental and calculated I(E) curves.

All the R-factor analyses in this work were done with the Pendry R-factor (R_p), which uses first derivatives and is cheaper than the use of
the Zanazzi-Jona R-factor. Pendry's multi-beam R-factor can be expressed as

$$ R_p = \frac{\sum_i (Y_i \text{ calc} - Y_i \text{ expt})^2 \, dE}{\sum_i (Y_i^2 \text{ calc} + Y_i^2 \text{ expt})\, dE} \quad (1.15) $$

where the summation is over the individual beams, the $Y_i$ are defined as

$$ Y_i = L^{-1}/(L^{-2} + V_{0i}^2) \quad (1.16) $$

where $L = d \ln I(E)/dE \quad (1.17)$

and $V_{0i}$ is the imaginary component of the constant muffin-tin potential used in the calculation.

Contour plots of R factors are often given as simultaneous functions of appropriate geometrical parameters and $V_{0r}$ in the calculations; these plots conveniently identify conditions for the lowest value of the R factor. Those geometrical conditions should closely pinpoint the actual surface structure provided that the R factor used is reliable. It is also important that errors are minimized in both the experimental and computational analyses, and that sufficient data are compared.
1.3 Auger Electron Spectroscopy (AES)

The emission of Auger electrons, as they have become known, was first recognized and explained by Pierre Auger in 1925 [37]. Auger emission involves three energy levels and the mechanism is shown in Figure 1.8. The first step involves supplying sufficient energy by either electron or photon impact to ionize an electron from an inner shell (e.g., the hole in K-shell of Figure 1.8). This vacancy can then be filled by an electron which drops down from a higher shell (e.g., L), and the excess energy (i.e., $E_k - E_L$) can be used either to emit a photon (e.g., X-ray emission) or to eject another electron (i.e., an Auger electron) from other levels (for the example in Figure 1.8 the Auger electron is emitted from L). This Auger electron possesses a kinetic energy approximately equal to $E_k - E_{L2} - E_{L3}$. In general Auger electrons have energies characteristic of the atoms from which they emerge; these energies are independent of the incident electron energy. This allows for their use in identifying all atoms of the periodic table except for hydrogen and helium which have insufficient electrons. Several reviews of the applications of AES have been published [38-42].

The competition between Auger emission and X-ray fluorescence depends on the energies of the transition. If the binding energy of the initial core level is less than about 2 keV, Auger electron emission is generally more probable than X-ray fluorescence. In this work the initial core level ionization is accomplished by electron impact. The sensitivity
Figure 1.8 Schematic indication of an Auger process to produce a $KL_2L_3$ Auger electron.
is generally optimized by having the incident beam energy about three times that of the inner shell ionization energy.

Auger electrons with kinetic energies in the approximate range 50 to 1000 eV have short mean free paths (Figure 1.2) in solids and this provides Auger spectroscopy with its surface sensitivity. In practice the Auger electrons are accompanied by a large number of secondary electrons, so the Auger contributions occur as small peaks on a large background in the \( N(E) \) curves (Figure 1.1). However the Auger peaks can be accentuated by differentiation, and \( dN(E)/dE \) curves are obtained electronically. This facilitates the recognition of Auger data from the background, which is high and slowly-varying. It is customary to catalog Auger energies by positions of the negative peaks in the first derivative spectra.

The use of AES for qualitative surface analysis is achieved by comparing measured spectra with standard representative spectra [43] or with tabulated energies [44]. The existence of several Auger energies for most elements (e.g. Auger energies at 92, 118, 147 and 174 eV for Zr) usually eliminates any ambiguity in assignment. Figure 1.9 compares Auger electron spectra for two zirconium surfaces; one is clean (b) and the other from the handbook (a) contains C and O contamination [43]. To avoid instrumental artifacts, adsorbate concentrations on a single crystal surface are frequently quantified by comparing values of the relative Auger peak height ratio of adsorbate to that of the substrate (see Chapter 3). A discussion of the use of Auger electron spectroscopy for surface quantitative analysis can be found in the book edited by Briggs and Seah [45].
Figure 1.9 Auger spectrum for zirconium surface.
(a) Standard zirconium spectrum from handbook [43].
(b) Measured after 50 hours of cleaning.
1.4 Aim of Thesis

The work described in this thesis represents a contribution to the development of the subjects of surface structural chemistry and LEED crystallography. Specific studies have been made for the adsorption of \( \text{C}_2\text{H}_4 \), CO and \( \text{PH}_3 \) on the (0001) surface of zirconium. The hope has been to complete LEED structure analyses for these systems.

Studies on the Zr(0001) surface are of interest because of the technological importance of zirconium, especially in the nuclear industry. This is due to its low absorption cross section for neutrons, as well as its high resistance to corrosive environments inside nuclear reactors [46,47]. There is only very limited data available on properties of its surfaces. Careful work has been inhibited by the very high reactivity of this metal, and by its limited availability. Also surface studies of zirconium are not helped by its bulk phase transition (hcp to bcc) at 820°C [48]. Light atom impurities have a strong tendency to diffuse into the bulk of this metal and in principle this could hinder control of material cleanliness.

An outline of this thesis is as follows. Chapter 2 describes the experimental background for these LEED and AES studies. Chapter 3 reports observations for the adsorption of \( \text{C}_2\text{H}_4 \) on the Zr(0001) surface and analyses of LEED beam intensities measured from the surface structures designated Zr(0001)-(1X1)-C. Chapter 4 details the investigations for the adsorption of CO on Zr(0001), and some comparisons are made with oxygen
adsorption on this surface. Chapter 5 describes the adsorption of PH$_3$ on the Zr(0001) surface. No quantitative LEED data could be obtained from this prepared surface; this study aimed to provide the first structural analysis for the adsorption of phosphorus on a transition metal surface.
Chapter 2

Experimental
2.1 Sample Preparation

This study used a (0001) surface of zirconium which was prepared from a single crystal rod which was provided by Dr. P.R. Norton (AECL, Chalk River Nuclear Laboratories). The initial orientation was found to be about 2° off the (0001) plane, and therefore it was necessary to reorient to within 0.5° by using the Laue back reflection method. The spark erosion technique (Agietron, Agie, Switzerland) was used to cut the sample, both to expose the desired plane, which was oriented perpendicular to the X-ray beam, and to ensure it had the proper size for the sample holder in this laboratory. The sample was then mounted in an acrylic resin ("Quickmount", Fulton Metallurgical Products Corp., U.S.A.) and glued to a polishing assembly equipped with alignment micrometers. During the polishing of the sample its orientation was checked and adjusted to minimize any deviation due to the cutting or polishing. The planetary lapping system (DU 172, Canadian Thin Film Ltd.) was used to polish the sample with progressively finer diamond paste from 9 to 3 micron. Finally, one-micron polishing was accomplished by hand using an artificial deer skin (Microcloth, Buchler 40-7218).

The whole jig with crystal assembly was then fixed to a lathe bench with a He/Ne laser (Figure 2.1) to check that the polished face was oriented to within 0.5° of the desired (0001) crystallographic plane. Once the orientation was found to be satisfactory, the sample assembly was immersed in acetone to dissolve the resin and free the sample. The sample was then chemically etched for 30 s in acid solution (45% HNO₃, 50% H₂O, 5%
for large $R$, 

$$\frac{r}{2R} = \theta \text{ (rads)}$$

Figure 2.1 Use of laser beam deflection method to measure the angular misalignment ($\theta$) between the physical plane and the crystal plane of interest which had previously been oriented by the back reflection technique.
HF by volume [49]). Finally the sample was degreased in trichloroethylene, acetone, methanol and distilled water in an ultrasonic bath and then dried and mounted in a sample cup with a resistance heater (Varian 981-2058). A 0.005" chromel-alumel thermocouple was spot-welded on to the top of the sample cup for monitoring the temperature of the sample.

2.2 UHV Chamber and Other Facilities

The experiments in this work were carried out in a Varian FC 12 vacuum chamber, which is made of non-magnetic stainless steel components joined together by knife-edge flanges with copper gaskets. Figure 2.2 shows the top view of this chamber, which is equipped with conventional hemispherical 4-grid LEED optics (Varian 981-0127) as well as a single-pass cylindrical mirror analyzer (Varian 981-2607) and a glancing incidence electron gun (Varian 981-2454). The chamber has other facilities including an argon ion gun (Varian 981-2043), a window for observing the sample position and diffraction pattern, a nude ion gauge to monitor the pressure, a manipulator (Varian 981-2530), and a nozzle gas doser connected to a variable leak valve for applying gases to the sample and for introducing argon for ion sputtering.

The manipulator is equipped with a flip assembly (Varian 981-2532) which includes a sample heater. The manipulator flange has a pair of liquid nitrogen feedthroughs and several electrical feedthroughs mounted on it which can be used for cooling or heating the sample as well as measuring the temperature by means of the thermocouple. The feedthrough to
Figure 2.2 Schematic diagram of the FC12 UHV chamber.
thermocouple can also be used to monitor the ion current during Ar$^+$ bombardment. Additionally, the manipulator allows the sample to be rotated around a vertical axis and displaced along the three Cartesian coordinates. The flip assembly allows the sample to be rotated by up to around ± 20° about an axis parallel to the surface plane.

The pumps in this chamber are a main ion getter pump (200 Ls$^{-1}$), an oil diffusion pump, a titanium sublimation pump, and a pair of sorption pumps (Figure 2.3). Also a small ion pump (20 Ls$^{-1}$) is used on the gas handling line. The pump down of the main chamber from atmosphere starts with liquid nitrogen cooling of the sorption pump. This can evacuate the chamber to $10^{-2}$ Torr; further pumping to $10^{-7}$ Torr is accomplished with the water-cooled and liquid-nitrogen-trapped diffusion pump. At this point the UHV ion pump can be turned on to achieve a pressure of $10^{-8}$ Torr. To reduce the pressure to the $10^{-11}$ Torr range, the chamber must be baked to desorb the excess gaseous molecules like water which are adsorbed on the walls of the chamber. Typical baking conditions are 200°C for 10-12 hours with the titanium sublimation pump turned on to help pump away these desorbed gases. After baking, all the filaments (e.g. ion gun and electron gun) are degassed while the chamber is still hot (about 80°C). The gas side line can be baked with wrap-around heating tapes, and a pressure of about $10^{-7}$ Torr can be obtained.
Figure 2.3 Diagrammatic representation of the pumping system.
2.3 Sample Cleaning in the UHV Chamber

After the chamber was evacuated to $10^{-8}$ Torr using the procedure described in Section 2.2, it is important to sputter-etch the zirconium surface with a short and gentle argon ion bombardment before baking the chamber. Such a treatment helps eliminate many impurities that may have been left over on the surface during the sample preparation procedure, and which may otherwise diffuse into the sample during the baking. This is particularly important for such a reactive and absorbing sample like zirconium.

The Ar$^+$ bombardment is done with the main ion pump off, and high-purity argon (Matheson 99.9995%) is introduced into the chamber until the pressure is approximately $5 \times 10^{-5}$ Torr. The initial gentle Ar$^+$ bombardment was done with the gun voltage set at about 600 V, and the ion current measured between sample and ground was maintained at 3 to 4 μA. During the Ar$^+$ bombardment, the titanium sublimation pump is used both to pump away impurities sputtered off from the surface and to maintain the purity of the argon gas. After a few hours of ion bombarding, the argon is pumped away by the diffusion pump and then the main ion pump is switched on to bring the vacuum back to normal.

After the initial Ar$^+$ bombardment and baking following the sample cool down to room temperature, the main surface cleaning operations can start. These operations include cycles of Ar$^+$ bombardment followed by
annealing. The annealing aims to reorder the surface after the damage caused by the ion bombardment. Vigorous bombardment will result in much surface damage. A careful balancing of bombardment and annealing conditions is required since higher annealing temperatures may also cause problems with impurity segregation or diffusion. The key to obtaining a clean and well-ordered surface is to understand the behaviors of all the impurities on the surface as a function of temperature. Some information was obtained from Foord et al [50] and P. Wong [51]. The experience of these other authors helped me to decide appropriate recipes. Specifically the Ar$^+$ bombardment of zirconium was done with an ion energy of 2 keV (current density up to 5 μA, 10 hours per cycle); the annealing was done by heating the sample to about 600°C and then immediately cooling to room temperature. In both cases the rate of temperature change was about 1°C per second.

After each cycle of ion bombardment, AES was used to assess impurities on the sample. The Auger electron spectra for the surface cleaned by about 50 hours of Ar$^+$ bombardment and annealing to 600°C is shown in Figure 1.9(b). A clean well-ordered surface is also characterized by a sharp (1X1) LEED pattern with low background.

2.4 Auger Electron Spectroscopy

The experimental arrangement for obtaining Auger spectra is illustrated in Figure 2.4. A glancing incidence electron gun was used with energy around 2 keV; the low angle of incidence gives better surface sensitivity than normal incidence. The cross sectional area of the
Figure 2.4 Schematic diagram of the experimental set-up for Auger electron spectra using a cylindrical mirror analyzer and glancing incidence electron gun.
electron beam is about 1 mm$^2$. The Auger electrons emitted from the surface are detected by the single-pass cylindrical mirror analyzer (CMA). This is a dispersive-type analyzer [4] which consists of two coaxial cylindrical electrodes and a channel electron multiplier. The inner cylinder has appropriately positioned slits and it is grounded. A variable repulsive voltage $V_r$ can be applied to the outer cylinder, thereby allowing only electrons having a narrow energy range $E \pm \Delta E$ to pass through the slits on the cylinders and be focussed electrostatically on to the electron multiplier. By simultaneously sweeping the voltage $V_r$ on the outer cylinder and measuring the current collected, the energy distribution curve of the electrons is obtained. In order to increase the signal-to-noise ratio, the energy distribution is differentiated (i.e., $dN(E)/dE$). This is accomplished by applying a small modulation voltage $U_m \sin \omega t$ ($U_m = 10 V$, $\omega = 17$ kHz) on $V_r$. The modulated signal at first harmonic on the multiplier, detected by a lock-in-amplifier is proportional to $dN(E)/dE$ [52].

2.5 LEED Experiment

2.5.1 LEED Optics

The conventional LEED optics on the system used consist of four hemispherical high transmission grids, a phosphor coated screen and an integral electron gun as shown in Figure 2.5. The gun produces electrons by heating a filament and the energy of the electron beam is determined by the potential difference between the filament and the sample (which is grounded). The gun has a set of focussing elements, and the beam diameter
Figure 2.5 Schematic diagram of electron optics used for LEED experiments.
at the sample is about 1 mm. The typical energies used in this work are between 40 to 250 eV, the beam current was kept at approximately 1 μA for energies above 100 eV, and it linearly declines to about 0.2 μA as the energy is reduced below 100 eV to its lowest value (e.g. 40 eV). This variation in beam current must be noted for normalizing the measured LEED intensities.

The elastically back scattered electrons from the sample pass through all four hemispherical concentric grids (i.e., $G_1$ to $G_4$ in Figure 2.5) and are accelerated on to the fluorescent screen which has a positive potential (about 5 kV). Each diffracted beam will give a spot on the screen, and the set of spots form a diffraction pattern. The grid $G_1$ is grounded, as are the sample and drift tube of the electron gun, to ensure that the scattered electrons travel in a field free region between the sample and $G_1$. The grids $G_2$ and $G_3$ are connected together and are held at a negative potential which is slightly smaller than the accelerating voltage in order to eliminate most of the inelastically scattered electrons. The fourth grid $G_4$ is grounded to screen $G_2$ and $G_3$ from the high voltage on the collector screen, and to reduce capacitance effects.

2.5.2 LEED Intensity Measurements

A commercial video LEED analyzer (Data-Quire Corp., Stony Brook, N.Y.) accompanied with a TV camera (COHU 4410/ISIT) was used to measure the intensities of diffraction spots displayed on the fluorescent screen. Figure 2.6 shows a schematic diagram of the system for measuring LEED intensities in real time. The ISIT camera basically contains a
Figure 2.6 Schematic diagram for the TV analyzing system.
photocathode tube and a silicon target. The LEED pattern image from the screen is focussed through the lens on to the photocathode tube, then the emitted photoelectrons are accelerated to the silicon target to produce the enhanced output signal. This effect can allow a reduction in the incident beam current required for producing a measurable LEED pattern, and thereby reduce the possibilities for unwanted electron-beam effects during the measurements. This method can measure diffracted beam intensities much faster than the more traditional methods which use a Faraday cup collector or a spot photometer [53,54].

A 32K microprocessor (Motorola 6800) controls the digitization of the video signal from the camera and the LEED gun voltage via a D/A converter. Each camera frame consists of 256x256 pictures (or pixels), and a 10x10 pixel window is used to define the region to be digitized. The intensity of each LEED spot is obtained by adding the intensities of all 100 pixels within the window. They can be controlled manually by setting the gain level in the range between 0 and 225. The scanning of each single frame is completed in 1/60 s, while the complete frame to be digitized needs 256/60 s.

The VLA system provides up to 49 isolated windows for digitizing the LEED spots simultaneously for each frame (i.e., at a fixed energy). Once a frame is digitized, the next frame appears after changing the incident beam energy and the window is automatically matched to the new spot position for the next digitization process. This matching is done by the computer using previously supplied information on unit mesh dimensions and direction of
incidence. The effect of background can be minimized by appropriately setting the contrast level; in practice it is often better to measure fractional beams and integral beams separately with different gain level settings.

The measured \( I(E) \) curves are normalized with respect to the incident beam current,

\[
I = I' / I_0,
\]

where \( I' \) and \( I_0 \) are the raw diffracted beam intensity and incident beam currents respectively. In the experiment, the incident beam for LEED is chosen to coincide with a symmetry element of the surface structure, so the diffraction pattern exhibits symmetrically related beams. Figure 2.7 shows \( I(E) \) curves measured for five beams from a Zr(0001)-(1x1)-C surface; these are essentially equivalent which confirms that the incidence direction is very close to normal. This averaged curve is then smoothed with two cubic spline operations to provide the final experimental \( I(E) \) curve [55].

2.5.3 Spot Profile Method

In this work, the intensity measurement of a LEED spot involves summing the digitized intensities of the 100 pixels in the window covering the spot. The spot profile measurement, by contrast, measures the intensity distribution across the diffraction spot. This measurement at fixed energy, especially for fractional beams, can provide information
Figure 2.7 Five equivalent (1,1) beams from Zr(0001)-(1x1)-C surface at normal incidence. They are averaged and finally smoothed.
Figure 2.8 LEED spot profile measurement:
(a) LEED spot covered by 10x10 pixels window,
(b) intensity of spot plotted versus window width (x).
about conditions for surface order and disorder [56]. The spot profile measurement is outlined in Figure 2.8. In Figure 2.8(a) the spot is covered completely by the window, while in Figure 2.8(b) the intensity profile along $X_{\text{win}}$ is recorded. The full-width at half-maximum (FWHM) is noted and its reciprocal can provide a helpful indication of surface order for varying experimental conditions. The value of FWHM therefore provides a quantitative measurement of spot sharpness and hence of the quality of a LEED pattern.
Chapter 3

Structures Formed by the Adsorption of $C_2H_4$ on the
(0001) Surface of Zirconium
3.1 Introduction

So far the chemisorption of ethylene on (0001) surfaces of hexagonal close packed metals has not yet been studied at the quantitative level, although limited qualitative observations have been reported including those for ethylene on the (0001) surfaces of rhenium [57,58], cobalt [59] and titanium [60]. Zirconium provides important materials in the nuclear industry; for example some compounds with carbon were studied earlier as high temperature materials [61]. Therefore carbonized zirconium has considerable technological interest [62,63]. Only very limited studies have been done for adsorption on well-characterized zirconium surfaces. Foord et al studied the dissociation and diffusion of CO, NO, N₂, O₂ and D₂ on polycrystalline samples [50]; they reported that O, N and C atoms migrate into the bulk on heating while H desorbs at about 700 K. Hoflund et al investigated the interaction between polycrystalline zirconium and H₂, O₂, N₂, CO and N₂O [67,68]; they reported that some specific sites are responsible for the chemisorption of nitrogen and oxygen on zirconium. Lin and Gilbert [69] reported that the sticking coefficient for hydrogen on polycrystalline zirconium is very low (maximum of about 6.5 x 10⁻⁴ near 700 K), an observation which may seem surprising in view of the well-known effectiveness of zirconium as a "getter" material for hydrogen. Other related studies include those by Tapping who studied the oxidation and hydriding reactions of polycrystalline Zr with XPS and UPS [47], and Wong in this laboratory who studied the chemisorption of O₂, H₂S, and N₂ on the
Zr(0001) surface by using LEED and AES [64-66]. Both oxygen and nitrogen show LEED patterns corresponding to (1x1) structures, apparently with O and N atoms occupying octahedral holes below the metal surface. A sharp (3x3) LEED pattern was observed with H₂S chemisorption. The present Chapter describes the use of LEED and AES to study the adsorption of C₂H₄ on the single crystal zirconium (0001) surface. Comparisons are made with the earlier work, and where appropriate surface structural information (e.g. bond length and bonding sites) are extracted.

3.2 Experimental

The apparatus and sample-cleaning procedures used in this work were as described in Chapter 2. The C₂H₄ gas (Matheson C.P.) was used as the carbon source. Each adsorption study was made on a surface which showed a sharp (1x1) LEED pattern, with hexagonal symmetry at normal incidence, and for which no contaminants were apparent with AES. The exposures were made at room temperature via a nozzle.

The relative amounts of adsorbed C₂H₄ (i.e., carbon) were assessed with the Auger peak height ratio

\[ R_c = \frac{A_{273}}{A_{92}} \]

(i.e., the ratio of the Auger peak height for carbon at 273 eV to that of zirconium at 92 eV), and the ratio
was also used to provide a supplementary monitoring of the cleanliness of the zirconium surface. The 92 eV Auger peak of Zr is a convenient reference because it involves electron emission from the inner shell, thereby making it less sensitive to surface contamination [50]; also it limits the influences of attenuation and shift/broadening effects which have been noted in valence spectra [50,70].

After each adsorption experiment, the sample surface was cleaned by Ar$^+$ bombardment and reordered by heating to 600°C followed by immediately cooling to room temperature. The LEED intensity-versus-energy (I(E)) curves were measured with a video LEED analyzer system (section 2.5.2) over the energy range 62-240 eV with constant increment of 2 eV.

3.3 Results and Discussion

3.3.1 $C_2H_4$ Adsorption and Heating Effects

The exposure of a clean, well-ordered Zr(0001) surface to about one Langmuir (1 L = 10$^{-6}$ Torr s) of C$_2$H$_4$ yielded a surface characterized with $R_c = 0.20$ and $R_{Zr} = 1.20$. With greater exposures to C$_2$H$_4$, the $R_c$ values could be correspondingly increased. Figure 3.1 shows part of the uptake curve measured for C$_2$H$_4$ at room temperature. Since it is known that carbon can migrate into the bulk on heating [50], an assessment of the bulk diffusion of carbon atoms from C$_2$H$_4$-treated Zr(0001) surfaces is needed to
Figure 3.1 Auger peak height ratio $R_c$ plotted as a function of $C_2H_4$ exposure time at $2 \times 10^{-7}$ Torr.
provide a basis for preparing well-characterized carbon-adsorbed structures. This was done as follows. The Auger peak ratios \( R_c^T \) and \( R_{Zr}^T \) were measured each time after flashing to temperature \( T \) K and immediately cooling back to room temperature. \( R_c^T \) was normalized by the initial value \( R_c^{\text{init}} \) (i.e., the value right after dosing \( C_2H_4 \) but before the heating was started), while \( R_{Zr}^T \) was normalized by 1.40 (the \( R_{Zr} \) value characterized for clean zirconium). Two plots of the normalized values \( (R_c^T/R_c^{\text{init}} \) and \( R_{Zr}^T/1.40 \) obtained for successively increasing \( T \) are shown in Figure 3.2, for which \( R_c^{\text{init}} \) equals 0.33. The first break in \( R_{Zr}^T/1.40 \) (Figure 3.2(b)) at around 400°C may be associated with the desorption of hydrogen. This follows a similar observation for \( H_2S \) chemisorption on Zr(0001) by Wong [65]; also Lin and Gilbert [69] reported that hydrogen desorbs from polycrystalline zirconium at around 700 K. The second break in \( R_{Zr}^T/1.40 \) which starts at 490°C apparently results from carbon diffusion into the bulk since it correlates with the change in slope for \( R_c^T/R_c^{\text{init}} \) shown in Figure 3.2(a). This temperature for the bulk diffusion of C into zirconium is some 50° and 250° higher than the corresponding values found earlier for N and O respectively [51].

The initial adsorption of \( C_2H_4 \) yielded a diffuse (1x1) LEED pattern with relatively high background (e.g. \( R_c = 0.20, R_{Zr} = 1.20 \)). With further brief heating to 470°C, a very sharp (1x1) LEED pattern was observed on cooling to room temperature. This heating temperature was chosen as being
Figure 3.2 Normalized Auger peak-height ratios (a) $R^T_C/R^\text{init}_C$ and (b) $R^T_{Zr}/1.40$ as a function of temperature for $C_2H_4$ adsorbed on Zr(0001). The initial coverage corresponds to $R^\text{init}_C = 0.33$ and $R^\text{init}_{Zr} = 1.15$; the final values of $R_C$ and $R_{Zr}$ are 0.00 and 1.40 respectively.
high enough to desorb hydrogen, but still sufficiently low that carbon bulk migration is not significant. Careful visual observations of the intensity distribution in the sharp (1x1) LEED patterns at normal incidence were compared with that of the clean Zr(0001) surface. As \( R_C \) was increased from zero, a new feature was established at \( R_C = 0.20 \), namely a bright region for the (1,1) beam between 132 and 136 eV. This differs from the clean surface where the (1,1) beam is dim for that particular energy range. This contrast is also apparent in the measured I(E) curves. A sequence of I(E) curves for the (1,1) beam with various \( R_C \) values (from 0 to 0.43) at normal incidence was measured as shown in Figure 3.3. As \( R_C \) increases, the changes in the I(E) curves from those of the clean surface are quite subtle until \( R_C = 0.20 \), but we believe that value marks a new well-defined (1x1)-C surface. Bigger changes occur as \( R_C \) increases beyond 0.20. With reference to the I(E) curves in Figure 3.3, the intensity of the carbon peak at around 136 eV increases very significantly, while the peak which is at 118 eV for \( R_C = 0.20 \) shifts to lower energy and is reduced to 112 eV when \( R_C \) equals 0.43. This evolution suggests a further higher-coverage (1x1)-C structure may form, although we have not studied this latter system beyond \( R_C = 0.43 \). Therefore we do not know whether that value completes the second (1x1)-C structure; nevertheless, it does correspond to a carbon coverage approximately twice that of the first (lower-coverage) (1x1)-C structure.

The I(E) curves measured for the intermediate coverages (e.g. \( R_C = 0.28 \)) can be well-reproduced by appropriately weighted mixtures of the curves for \( R_C = 0.20 \) and \( R_C = 0.43 \), assuming they come from the two
Figure 3.3 Comparisons of $I(E)$ curves for (1,1) beams from (1x1)-C surfaces with different $R_C$ values.
different (1x1)-C structures as noted above. This is shown for the (1,1) beam in Figure 3.4 which plots appropriately weighted $I(E)$ curves

$$I(\chi) = \chi I(R_C=0.20) + (1-\chi)I(R_C=0.43)$$

(3.1)

for a range of values of $\chi$ (between 0 and 1). The measured $I(E)$ curve for $R_C = 0.28$ agrees closely to that calculated with $\chi = 0.6$. This suggests that the surfaces with coverages between $R_C = 0.20$ and $R_C = 0.43$ involve appropriate mixtures of the low-coverage and the high-coverage (1x1) domains. By contrast, the $I(E)$ curves for $R_C = 0.28$ are not well-modelled by mixtures of $I(E)$ curves for the clean and $R_C = 0.43$ surfaces (Figure 3.5), an observation which provides further support for $R_C = 0.20$ defining a completed (1x1)-C structure. The latter structure appears analogous to the Zr(0001)-(1x1)-O and Zr(0001)-(1x1)-N surface structures which have been previously subjected to LEED crystallographic analyses [64,66].

$I(E)$ curves for the Zr(0001)-(1x1)-C structure with $R_C = 0.20$ were measured (Section 2.5.2) for the beams (1,0), (1,1), (2,0) at normal incidence and for the (0,0), (1,0), (0,1), (1,1), (2,0), (2,1), (2,2), (3,2), (3,3) beams with an incidence direction in which the polar angle is $14^\circ$ and the azimuthal direction is parallel to a mirror plane in the surface. Three independent $I(E)$ curves, namely (1,0), (1,1) and (2,0) were also measured at normal incidence for the Zr(0001)-(1x1)-C structure with $R_C = 0.43$. These beam notations are shown in Figure 3.6.
Figure 3.4 Measured I(E) curve of (1,1) beam from Zr(0001) - (1x1)-C with $R_c = 0.28$ compared with weighted mixtures of the curves for $R_c = 0.20$ and $R_c = 0.43$ according to equation (3.1) with $\chi$ varying from 0.0 to 1.0.
Figure 3.5 Measured I(E) curve of (1,1) beam from Zr(0001)-(1x1)-C with $R_c = 0.28$ compared with weighted mixtures of the curves for $R_c = 0.00$ (clean surface) and $R_c = 0.43$ according to Equation (3.1) with $\chi$ varying from 0.0 to 1.0.
Figure 3.6 Reciprocal net and beam notation for the Zr(0001)-(1x1)-C structure.
3.3.2 Calculations

All structural models considered in the LEED intensity analyses for this study were built from the stacking of hexagonal close-packed layers of either C atoms or Zr atoms. Sixteen different models were considered. These models are identified by the usual A.B.C notation for close-packed zirconium layers which are laterally displaced with respect to each other so that the hcp and fcc structures follow respectively the familiar stacking sequences ABAB*** and ABCABC***. This notation is extended so that the same symbols in parentheses have the analogous meaning for carbon. For example, the model type (B)A(C)BAB***, as is shown in Figure 3.7, indicates zirconium with the unreconstructed stacking sequence while C atoms occupy both overlayer and underlayer sites (these are respectively the "expected" 3-coordinate sites and octahedral hole sites between the first and second metal layers).

The models considered in this structural analysis are classified according to the following seven categories:

1) Simple overlayer models where carbon atoms occupy 3-fold coordination sites above the unreconstructed zirconium surface (i.e., models designated (B)ABAB*** and (C)ABAB***).

2) Graphitic overlayer models where carbon atoms occupy both hcp and fcc type positions on the surface as in the model [(B)+(C)]ABAB***.

3) Octahedral underlayer structures where carbon atoms occupy octahedral holes within an unreconstructed zirconium structure. Variations of this model are designated A(C)BABA***, A(C)B(C)ABAB***, A(C)B(C)A(C)B*** according to whether the carbon atoms occupy all
Figure 3.7  Partial view of the Zr(0001)-(1x1)-C structure corresponding to the model designated (B)A(C)BAB\ldots.  Atoms in the topmost Zr layer are in A-type positions (open solid circles), while the second Zr layer has atoms in B-type positions. The carbon overlayer (smaller darker circles) has atoms in B-type positions while the underlayer C atoms (smaller shaded circles) occupy the octahedral holes in C-type positions.
octahedral holes respectively between the first and second metal layers, between the first three metal layers, between all metal layers probed by LEED.

(4) Octahedral underlayer structures where C atoms occupy the octahedral holes between those zirconium layers which have reconstructed to a local fcc-type packing arrangement (e.g. C(B)A(C)BA•••).

(5) Tetrahedral underlayer structure where C atoms occupy all tetrahedral holes between the first and second zirconium layers (i.e. model referred as A(Bt)(At)BA•••, where the symbols (Bt) and (At) indicate carbon atoms located respectively directly above atoms in the second zirconium layer and directly below atoms in the topmost zirconium layer.

(6) Graphitic underlayer structure where C atoms occupy two octahedral holes between the first and second zirconium layers which have locally reconstructed to the simple hexagonal packing arrangement (i.e. model designated as B[(A)+(C)]BA•••).

(7) Overlayer plus octahedral underlayer structures (e.g. (B)A(C)BA••• or[(A)+(C)]B(C)ABB•••).

For each model type, the calculations treated the neighboring Zr-C interlayer spacing ($d_{Zr-C}$) as a variable. This parameter was varied from 0.60 to 1.20 Å for simple overlayer carbon, from 0.80 to 1.40 Å for graphitic overlayer carbon, from 1.52 to 1.82 Å for graphitic underlayer carbon, and from 1.14 to 1.50 Å for simple octahedral type underlayer carbon. However, for models of category (7), the underlayer Zr-C inter-
layer spacing was fixed at 1.36 Å, which is close to values suggested by the results below. For the tetrahedral underlayer structure (i.e. A(Bt)(At)BAB... shown in Figure 3.8), the specific interlayer spacings (i.e., $d_{\text{Zr-C}}$ and $d_{\text{C-C}}$) were designated as in Table 3.1. They must satisfy the equation

$$x^2 + 2xy = 3.49 \quad (3.2)$$

where $x$ and $y$ are $d_{\text{C-C}}$ and $d_{\text{Zr-C}}$ respectively. The Zr-C bond distance is $x + y$, and the Zr-Zr interlayer spacing ($d_{\text{Zr-Zr}}$) is $x + 2y$. For all models the directly neighbouring Zr-Zr interlayer spacings were kept at the value 2.57 Å for zirconium metal [72].

The multiple-scattering calculations used standard procedures [29,30]. The scattering by the zirconium structures, including incorporated carbon layers, was determined with the renormalized forward scattering method, while the carbon overlayers were added with the layer doubling method or the combined space method. All computational details followed those used in the previous analyses from this laboratory for Zr(0001)-(1x1)-O [64] and Zr(0001)-(1x1)-N [66].

The atomic phase shifts for carbon (up to $l = 7$) were calculated from an atomic potential model by superposing the charge densities of carbon atoms arranged on a body-centered cubic lattice with the lattice parameter 1.829 Å for carbon in octahedral-type sites and 1.455 Å for carbon in tetrahedral-type sites. In the calculations for the normal
Figure 3.8 Notation used to discuss the tetrahedral hole underlayer structure for Zr(0001)-(1x1)-C.
Table 3.1: Geometrical parameters used for model designated A(Bt)(At)BABABA••

<table>
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<tr>
<th>C-Zr bond distance</th>
<th>y = d_{Zr-C}</th>
<th>x = d_{C-C}</th>
<th>d_{Zr-Zr}</th>
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<td>1.511</td>
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</table>
incidence data, the 3-fold rotation and mirror reflection symmetries were utilized, while at off-normal incidence only the single mirror reflection plane could be used. The real part of the constant potential $V_{Or}$ between the muffin-tin spheres was set initially at -10.0 eV, and the imaginary potential ($V_{01}$) was fixed at -5.0 eV.

3.3.3 Structural Analysis for the Zr(0001)-(1x1)-C Surface with $R_c = 0.20$.

The levels of correspondence between experimental and calculated $I(E)$ curves were assessed both visually and with the reliability index ($R_p$) proposed by Pendry [36]. An initial pruning out of some less favored models was made by comparison with just the normal incidence data for $R_c = 0.20$ and contour plots of $R_p$ were made as a function of Zr-C interlayer spacing and the real part of the constant muffin-tin potential ($V_{Or}$). Values of $d_{Zr-C}$ which minimize $R_p$ for the normal incidence data are reported in Table 3.2, and those corresponding $I(E)$ curves are shown in Figure 3.9.

Some conclusions from the results in Table 3.2 are:

(1) Overlayer models, graphitic models and tetrahedral models are unfavored compared with underlayer models.

(2) There is no support, for the conditions of our surface preparation, for the combined overlayer/underlayer models.

(3) The most favored surface structure have C atoms occupying octahedral hole sites below the surface.
Figure 3.9 The I(E) curve from experiment (dashed line) for (1,1) beam from Zr(0001)-(1x1)-C with $R_0 = 0.20$ at normal incidence and compared with calculated curves for the 16 models listed in Table 3.2.
Figure 3.9 continued
Table 3.2  Values of Zr-C interlayer spacings and $V_\text{or}$ corresponding to minima in contour plots of $R_\sigma$ with normal incidence $I(E)$ curves for sixteen structural models of Zr(0001)-(1x1)-C with $R_\sigma = 0.20$.

<table>
<thead>
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<th>Model</th>
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<th>$V_\text{or}$ (eV)</th>
<th>$R_\sigma$</th>
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</thead>
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<td>1</td>
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<td>12.81</td>
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<tr>
<td>2</td>
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<td>1.38</td>
<td>15.41</td>
</tr>
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</tr>
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</tr>
<tr>
<td>10</td>
<td>(C)ABAB...</td>
<td>1.19</td>
<td>7.41</td>
</tr>
<tr>
<td>11</td>
<td>(C)B(C)ABAB...</td>
<td>1.19</td>
<td>13.47</td>
</tr>
<tr>
<td>12</td>
<td>(A)B(C)ABAB...</td>
<td>0.72</td>
<td>13.59</td>
</tr>
<tr>
<td>13</td>
<td>[(C)+(A)]BABA...</td>
<td>1.05</td>
<td>2.31</td>
</tr>
<tr>
<td>14</td>
<td>[(C)+(A)]B(C)ABAB...</td>
<td>1.10</td>
<td>4.81</td>
</tr>
<tr>
<td>15</td>
<td>B[(A)+(C)]BABA...</td>
<td>1.53</td>
<td>9.62</td>
</tr>
<tr>
<td>16</td>
<td>Tetrahedral (two sites)</td>
<td>1.08</td>
<td>12.56</td>
</tr>
</tbody>
</table>
Table 3.3 Values of Zr-C interlayer spacings and $V_{or}$ corresponding to minima in contour plots of $R_p$ for final structural models of Zr(0001)-(lxl)-C for $R_c = 0.20$ using experimental intensity curves at both normal and off normal incidence.

<table>
<thead>
<tr>
<th>Model</th>
<th>$d_{Zr-C}$ (Å)</th>
<th>$V_{or}$ (eV)</th>
<th>$R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A(C)BABA</td>
<td>1.33</td>
<td>12.00</td>
<td>0.315</td>
</tr>
<tr>
<td>2 A(C)B(C)AB</td>
<td>1.32</td>
<td>12.60</td>
<td>0.315</td>
</tr>
<tr>
<td>3 C(B)A(C)BA</td>
<td>1.28</td>
<td>8.69</td>
<td>0.383</td>
</tr>
<tr>
<td>4 f.c.c. bulk</td>
<td>1.27</td>
<td>8.00</td>
<td>0.388</td>
</tr>
<tr>
<td>5 h.c.p. bulk</td>
<td>1.32</td>
<td>13.30</td>
<td>0.320</td>
</tr>
</tbody>
</table>
Those more-likely models were further assessed by combined data for normal and off-normal incidence and appropriate values of $d_{\text{Zr-C}}$ which minimize $R_p$ are reported in Table 3.3.

From Table 3.3 the best correspondence between experimental and calculated $I(E)$ curves for the Zr(0001)-(1x1)-C surface with $R_c = 0.20$ is for models in which carbon atoms occupy all octahedral holes between unreconstructed layers of zirconium metal. However, the present analysis is unable to distinguish between the models involving a single carbon underlayer immediately below the zirconium surface and those with carbon incorporated several layers deep for the probe depth of LEED. The contour plots of $R_p$ for these models as a function of $d_{\text{Zr-C}}$ and $V_{0r}$ are shown in Figure 3.10; the minimum in $R_p$ indicates the condition for best correspondence between the calculated and experimental $I(E)$ curves. The actual carbon-on-zirconium surface studied here could be attributed to single-, double-, and even multi-underlayer domains, perhaps with regions of only partial order. Comparison of $I(E)$ curves for the various diffracted beams are shown in Figure 3.11 for the model designated A(C)BAB\ldots. Table 3.3 reports for this model that the value $d_{\text{Zr-C}}$ equals 1.33 Å which corresponds to a Zr-C bond length of 2.30 Å using the lateral Zr-Zr distance for the (0001) plane in bulk zirconium [72]. This value is close to that of (2.34 Å) in bulk ZrC [73] as determined by X-ray diffraction.
Figure 3.10 Contour plot for Zr(0001)-(1x1)-C of $R_p$ versus $V_{0t}$ and Zr-C interlayer spacing for the structural model $A(C)BABAB\cdots$ appropriate to the surface with $R_C = 0.20$. 
Figure 3.11 Experimental I(E) curves (dashed lines) from Zr(0001)-(1x1)-C for $R_c = 0.20$ and compared with the calculated curves for the model A(C)BAB... with $d_{Zr-C}$ equal to 1.32 Å (upper continuous line) and 1.38 Å (lower continuous line).
Figure 3.11 continued
Figure 3.11 continued
3.3.4 Preliminary Analysis for the Zr(0001)-(1x1)-C Structure with $R_c = 0.43$.

Visual comparisons of the calculated and experimental $I(E)$ curves from the higher-coverage Zr(0001)-(1x1)-C surface structure indicates a tentative level of correspondence for the tetrahedral underlayer structure with the Zr-C interlayer spacing around 0.97-1.07 Å and with the C-C interlayer spacing between 1.13 and 1.08 Å (see Figure 3.8). Comparisons for the various diffracted beams are shown in Figure 3.12 for these structures. Some differences between the experimental and calculated $I(E)$ curves may result from disordered features, including some remnant occupation of octahedral holes. Nevertheless the present preliminary LEED analysis suggests a tendency for the higher coverages of carbon atoms to occupy tetrahedral holes below the surface (in lieu of forming graphitic underlayer or overlayer structures or growing an overlayer combined with octahedral underlayer structures). Studies have not yet been made in other related contexts of high coverages on Zr(0001), for example with oxygen, for which ZrO$_2$ is ultimately the favored product.

3.4 Conclusions

For the lowest-coverage Zr(0001)-(1x1)-C surface structures, the carbon atoms occupy octahedral hole sites between the first and second layers of zirconium metal, with the Zr-C interlayer spacing equal to 1.33 Å
Figure 3.12 Experimental I(E) curves (dashed lines) from Zr(0001)-(1x1)-C for $R_c = 0.43$ and compared with those calculated for the tetrahedral underlayer model with $d_{Zr-C}$ is equal to 0.96 Å (upper continuous line) and 1.06 Å (lower continuous line).
and this gives a Zr-C bond length equal to 2.30 Å. The model designated A(C)BABA for the lowest-coverage Zr(0001)-(1x1)-C surface appears to repeat features reported by Wong et al for the Zr(0001)-(1x1)-N system [66], both bulk ZrN and ZrC adopt the NaCl lattice structure.

The LEED analysis regarding the high-coverage Zr(0001)-(1x1)-C surface structure (the $R_c$ value is approximately twice that of the lower-coverage form) suggests that the model designated A(Bt)(At)BA is favorable, where carbon atoms occupy both tetrahedral hole sites between the first two zirconium layers with the Zr-C bond length in the vicinity of 2.10 and 2.15 Å. The metal-metal interlayer spacing with interstitial C is then significantly expanded to between 3.07 and 3.22 Å (the value for the clean metal is 2.57 Å) [72]. This corresponds to a fluorite-like structure for bulk ZrC$_2$. 
Chapter 4

An Investigation of CO Adsorption on the Zr(0001) Surface with LEED and AES
4.1 Introduction

The chemisorption of CO on well-characterized surfaces of hexagonal close-packed metals has not been widely studied so far, although the investigations to date include those on Re(0001) [58], Ti(0001) [74] and Ru(0001) [75]. For the first, Zaera et al reported a complicated LEED pattern when the Re(0001) surface is saturated with CO at 150 K; this changes to a (2x2)-type pattern upon heating. Shih et al reported on Ti(0001) that a (2x2) LEED pattern is obtained with an initial dosing of CO at room temperature and that a (1x1) LEED pattern is observed with greater exposures to CO. They were unable to completely analyse their LEED data, but they suggested that the surface may involve formation of an underlayer. Michalk et al did a LEED determination of the structure of the Ru(0001)-(\sqrt{3}\times\sqrt{3})R30°-CO surface and they reported that the adsorbed molecules bond to single metal atoms in a linear configuration (Ru-C-O) perpendicular to the surface.

So far there have been no reports about the chemisorption of CO on the Zr(0001) surface, although some qualitative studies on polycrystalline zirconium were done by Foord et al [50], Hoflund [67,68], and Lin [69]. These authors concluded that CO adsorbs dissociatively at room temperature, and that heating causes the chemisorbed species to diffuse into the zirconium bulk. However, hydrogen and deuterium also desorb from the surface at around 700 K. Wong et al in this laboratory studied the chemisorption of oxygen on the Zr(0001) surface [64], and they reported that a Zr(0001)-(2x2)-O surface was formed initially and then a Zr(0001)-(1x1)-O
surface after greater exposures to oxygen. LEED crystallographic investigations suggested that oxygen atoms occupy octahedral holes below the top layer of zirconium.

An interest of the current study of the adsorption of CO on the Zr(0001) surface is to compare with my investigation of the structural chemistry of adsorbed carbon (Chapter 3), and with the earlier work from this laboratory for the adsorption of oxygen. This Chapter describes the use of Auger electron spectroscopy and qualitative LEED for preparing structures formed by exposing a Zr(0001) surface to CO at room temperature. Quantitative LEED measurements are also made with the objective of providing a basis for future surface structural analyses.

4.2 Experimental

The apparatus and initial cleaning procedures used were as described in Chapter 3. A cleaned surface, which has no significant contaminants detectable by AES and for which LEED shows a sharp (1x1) pattern with hexagonal symmetry at normal incidence, was exposed at room temperature to CO gas (99.99% Matheson research grade) via a nozzle. For various exposures of the adsorbing gas, the relative amounts of adsorbed species were assessed with appropriate Auger peak height ratios; specifically \( R_O \) and \( R_C \), where

\[
R_O = \frac{A_{510}}{A_{92}}
\]
(A_{510} and A_{92} are the Auger peak heights for O and Zr at 510 eV and 92 eV respectively) and R_c is the same as used in Chapter 3. After each adsorption experiment, the sample surface was cleaned by Ar^+ bombardment and re-ordered by raising the temperature to 600°C followed by immediate cooling. I(E) curves were measured with a video LEED analyzer as described in Chapter 2.

4.3 Results and Discussion

4.3.1 Carbon and Oxygen Diffusion on Heating

The onset of the effective surface depletion of both carbon and oxygen atoms from a CO treated Zr(0001) surface was assessed by following the R_c and R_o values measured at room temperature after heating to progressively higher temperatures (Chapter 3) and cooling back to room temperature (we use R^T_c and R^T_o to indicate the ratios measured after heating to temperature T K). Figure 4.1 shows the plots obtained for the normalized ratios (R^T_o/R_o^{\text{init}}) and (R^T_c/R_c^{\text{init}}) (where R_o^{\text{init}} and R_c^{\text{init}} are the initial ratios, i.e. before the heating is started). The data in Figure 4.1 apply to a surface which was initially characterized with R_c = 0.36, R_o = 0.18; there is an initial depletion at around 140°C which appears to be associated with CO desorption [50]. By contrast the bulk diffusion of oxygen and carbon apparently starts at around 270°C and 490°C respectively. The latter value is consistent with the value obtained in Chapter 3 for carbon depletion from the initial C_2H_4 source, but the value
Figure 4.1 Normalized Auger peak-height ratios as a function of temperature for both carbon and oxygen. The initial surface of Zr(0001) is characterized with $R_c = 0.36$ and $R_o = 0.18$ after exposure to CO.
for oxygen is about 40°C higher than that (236°C) reported by Wong et al [64] for the Zr(0001)-O system. The latter therefore indicates that the presence of C atoms slightly slows the oxygen diffusion; apparently, then, there can be an attractive interaction between C and O within the surface region.

4.3.2 LEED Observations for (2x2)-CO Structure

Exposure of a clean, well-ordered Zr(0001) surface to about 1 L of CO at room temperature gave adsorption of both atomic constituents ($R_c = 0.28$, $R_o = 0.10$), but no extra LEED beams were immediately detectable. However, a poorly developed (2x2) LEED pattern was observed on heating to 240°C followed by cooling to room temperature. On heating to 480°C, a Zr(0001)-(1x1)-C surface was obtained with $R_c = 0.26$, $R_o = 0.00$. When this surface was re-exposed to pure oxygen (Linde, Specialty Gas) and annealed to 270°C, a faint (2x2)-C+O pattern was recovered after cooling back to room temperature. This surface appeared very similar to the (2x2)-CO LEED pattern. It is believed that the half-order beams in the (2x2)-CO LEED pattern result especially from the oxygen. This is fully consistent with the conclusion drawn from Chapter 3 that carbon adsorption only gives a (1x1) LEED pattern.

4.3.3 LEED Observations for (1x1)-CO Surface

With greater initial exposures of CO only (1x1) patterns were found, and these patterns were best established after heating to 270°C,
then cooling back to room temperature. \( \text{I(E)} \) curves were measured from such a prepared surface with \( R_C = 0.44 \), \( R_o = 0.18 \) for the beams \((1,0)\), \((1,1)\), \((2,0)\) at normal incidence and for the \((0,0)\), \((2,\bar{1})\), \((1,0)\), \((2,\bar{2})\), \((0,1)\) beams at off-normal incidence with \( \theta = 12^\circ \) and \( \phi = 90^\circ \). These \( \text{I(E)} \) curves are shown in Figure 4.2; they contain relatively high background contributions. The beam labels are the same as those indicated in Figure 3.6.

On heating surfaces with different amounts of CO adsorption to 470°C, all oxygen diffuses into the bulk and only carbon is left on the surface. All these surfaces showed \((1\times1)\) LEED patterns. The \( \text{I(E)} \) curves of the \((1,1)\) beams at normal incidence are shown in Figure 4.3 for different carbon coverages. A shoulder is formed at around 128 eV with \( R_C = 0.26 \), and as the carbon coverage increases further this shoulder develops into a full peak (e.g. at \( R_C = 0.44 \)). These trends are consistent with those observed in Chapter 3 when Zr(0001)-(\(1\times1\))-C was formed with different amounts of \( \text{C}_2\text{H}_4 \) adsorption. It appears for a comparable carbon coverage that the \((1\times1)\)-C surfaces are very similar, whether prepared initially from CO or from \( \text{C}_2\text{H}_4 \) (see results in Figures 4.4 and 4.5 for the \((1,1)\) beam at normal incidence for \( R_C = 0.26 \) and \( R_C = 0.31 \) respectively).

### 4.3.4 Domain Structure

In the case of low CO coverage (e.g. \( R_o = 0.10 \), \( R_C = 0.28 \)) only faint \((2\times2)\)-CO patterns are observed, when \( R_o \) is below the value of 0.16 which optimizes the \((2\times2)\) LEED pattern for the adsorption of oxygen alone [64]. By contrast in the case of higher CO coverage (e.g. \( R_C = 0.44 \), \( R_o = \))
Figure 4.2 Measured I(E) curves for Zr(0001)-(1x1)-CO with $R_c = 0.44$, $R_o = 0.18$ at normal and off-normal incidence directions.
Figure 4.2 continued
(1,0) beam $\theta=12^\circ \phi=90^\circ$

(2,-2) beam $\theta=12^\circ \phi=90^\circ$

(2,0) beam $\theta=12^\circ \phi=90^\circ$

Figure 4.2 continued
Figure 4.3 Comparisons of I(E) curves for (1,1) beams from different Zr(0001)-(1x1)-C surfaces with different $R_c$ values.
Figure 4.4 Comparison of I(E) curves for (1,1) beams from Zr(0001)-(1x1)-C surfaces with comparable $R_C$ values but prepared from CO and from $C_2H_4$, where $R_C = 0.26$ and $R_C = 0.28$ respectively.

Figure 4.5 Comparison of I(E) curves for (1,1) beams from Zr(0001)-(1x1)-C surfaces with comparable $R_C$ values but prepared from CO and from $C_2H_4$, where $R_C = 0.31$ and $R_C = 0.33$ respectively.
0.18), it was not possible to get a (2x2) LEED pattern. Since all indications support atomic adsorption, it seems likely that these structures involve oxygen and carbon occupying different domains. In principle they could be related either vertically or laterally to each other. The former implies the oxygen may locate underneath a carbon layer. This would be consistent with oxygen's strong tendency to form underlayer structures at the (0001) surfaces of both zirconium [64] and titanium [74]. Also the carbon coverage could attenuate the oxygen Auger signal so effectively reducing the recorded \( R_o \) value for a given oxygen coverage compared with the situation when oxygen adsorbs alone. With lateral domains, the carbon region could tend to compress the oxygen domains, perhaps even preventing them forming a (2x2) pattern for the higher CO coverages. Incidentally Wong et al [65] reported that coadsorbed oxygen and \( H_2S \) can form separate (2x2)-O and (3x3)-S domains.

4.3.5 Discussion

I(E) curves of the (1,1) beam at normal incidence for different surface structures are plotted in Figure 4.6; included are the clean surface (a), the Zr(0001)-(2x2)-O surface with \( R_o = 0.16 \) (b), the Zr(0001)-(1x1)-C surface with \( R_C = 0.43 \) formed by the adsorption of \( C_2H_4 \) (c), the Zr(0001)-(1x1)-O surface with \( R_o = 0.23 \) (d) and the Zr(0001)-(1x1)-CO surface with \( R_C = 0.44, R_o = 0.18 \) (e) (the curves for surfaces with oxygen adsorption come from Wong's study [64]). One immediate question is whether the Zr(0001)-(1x1)-CO structure involves a distinctive structure or whether it is composed of separate (1x1)-O and
Figure 4.6 Comparison of $I(E)$ curve for (1,1) beam from:
(a) clean Zr(0001) surface; (b) Zr(0001)-(2x2)-O surface with $R_o = 0.16$; (c) Zr(0001)-(1x1)-C surface with $R_c = 0.43$ formed by the adsorption of C$_2$H$_4$;
(d) Zr(0001)-(1x1)-O surface with $R_o = 0.23$; and
(e) Zr(0001)-(1x1)-CO surface with $R_c = 0.44$, $R_o = 0.18$. 
Figure 4.7 Measured I(E) curve of (1,1) beam from Zr(0001)-(1x1)-CO with $R_c = 0.44$, $R_Q = 0.18$ compared with weighted mixtures of the curves for $R_c = 0.43$ and $R_Q = 0.23$ according to equation (3.1) with $\chi$ varying from 0.0 to 1.0.
(1x1)-C domains. A suggestion for the latter is provided by the I(E) curve for Zr(0001)-(1x1)-CO surface with $R_c = 0.44$, $R_o = 0.18$ having a peak at around 140 eV which is characteristic of the Zr(0001)-(1x1)-O surface.

To probe further, weighted averages of measured curves were studied as in Chapter 3. The I(E) curve of the (1,1) beam for the Zr(0001)-(1x1)-O surface with $R_o = 0.23$ and that for the Zr(0001)-(1x1)-C surface with $R_c = 0.43$ which comes from C$_2$H$_4$ adsorption are used. The results are shown in Figure 4.7. The (1x1)-CO curve with $R_c = 0.44$ and $R_o = 0.18$ is not adequately reproduced by a weighted average, and that suggests that the (1x1)-CO surface does not involve separate lateral (1x1)-C and (1x1)-O domains. Therefore a new structure may be formed, perhaps with vertical domains. In principle insight into these structures should be obtainable from further investigations with LEED crystallography.
Chapter 5

LEED and AES Studies of the Interaction of PH$_3$ with the Zr(0001) Surface
5.1 Introduction

The surface chemistry of adsorbed phosphorus-containing molecules has not been studied widely, although Greenlief et al [76] reported the coadsorption and interaction of \( \text{PH}_3 \) with \( \text{D}_2\text{O}, \text{H}_2, \text{O}_2 \) and \( \text{H}_2\text{O} \) on the Rh(100) surface, while Kiskinova et al studied the chemisorption properties of \( \text{PH}_3 \) on Ni(100) [77]. For the particular case of phosphorus adsorption on zirconium, there are so far no reports either for polycrystalline or single crystal surfaces. Therefore we are interested to explore the behaviour of \( \text{PH}_3 \) on Zr(0001) and to compare with our work on the \( \text{C}_2\text{H}_4 \) and CO adsorptions. The study reported in the present chapter used LEED and AES to probe the adsorption of \( \text{PH}_3 \) on the Zr(0001) single crystal surface. A (3x3)-P LEED pattern was obtained, although it was too faint and existed over too short an energy range (around 60 eV) to be suitable for a LEED crystallographic analysis. Nevertheless qualitative observations are still possible and they allow some comparison with the Zr(0001)-\( \text{H}_2\text{S} \) system reported previously by Wong et al in this laboratory [65].

5.2 Experimental

The apparatus and cleaning procedures used here were the same as those used in Chapters 3 and 4. The \( \text{PH}_3 \) gas [Matheson 99.999\%] was filled into a gas bottle with an attached cold finger which can be dipped into liquid nitrogen to liquefy the \( \text{PH}_3 \) gas and further purify it. Since \( \text{PH}_3 \) has explosive and toxic properties, special care must be taken to handle it
(for example it must be pumped by a rotary pump rather than a conventional sorption pump). Figure 5.1 indicates the procedure used to fill the gas bottle. The key point in this pumping procedure is to use a large amount of nitrogen gas to dilute the PH₃ in the exhaust line which is directly connected to the fumehood. The filling procedure includes three steps. First the whole side line and gas bottle is pumped by the sorption pump; this is followed by operating the small ion pump which reduces the pressure in the side gas line to 10⁻⁶ Torr. The second step is to flush the side line and gas bottle with PH₃ by controlling the regulator valve on the cylinder (or the leak valve on the gas side line). The PH₃ was filled into the gas bottle and side line until the pressure reached about 1 atmosphere. Then the PH₃ gas needs to be pumped away. Before doing that, nitrogen was flowed into the exhaust line of the rotary pump to purge the residual air. The nitrogen flow (5 L min⁻¹) was maintained until the whole pumping procedure was finished. The nitrogen acts to isolate the PH₃ from air as well as to dilute it. The valve connected with the rotary pump could be opened to start pumping, and the pumping speed could be controlled by this valve and the leak valve; a slower pumping speed is preferred and the whole pumping will take about 1 hour to bring the vacuum back to 10⁻⁶ Torr. After the PH₃ gas was filled into the gas bottle and side line, the leak valve could be closed to separate the side line from the rotary pump and gas cylinder, and the rest of the PH₃ could then be pumped away by using the method described above.

After filling, the cold finger was immersed into the liquid nitrogen
Figure 5.1 Schematic diagram of the arrangement used for introducing \( \text{PH}_3 \) to the \( \text{PH}_3 \) gas bottle from the gas cylinder.
Dewar to liquefy the PH$_3$ gas from the gas bottle and the side line. After each use, this process could also be used to pump the excess PH$_3$ in the side line back to the gas bottle, and to purify the PH$_3$. This liquefaction allows a separation from other common gases, like N$_2$ and O$_2$, which can be pumped away by the small ion pump (the vapour pressure of PH$_3$ is about $10^{-6}$ Torr at 77 K) [78]. Several such condensation-pumping-warming steps were done until the liquid PH$_3$ becomes clear (which is the test used for sufficient purity).

The PH$_3$ gas was introduced on to a cleaned and well ordered Zr(0001) surface at room temperature via the nozzle as used in Chapters 3 and 4. For various exposures of PH$_3$, the phosphorus coverages on the surface are represented by the Auger peak height ratio

$$R_P = \frac{A_{120}}{A_{92}}$$

where $A_{120}$ is the peak height of the P Auger signal at 120 eV, which is overlapped with the Zr peak at 118 eV. After each adsorption experiment, the surface was cleaned by argon ion bombardment and reordered by heating to 600°C followed by cooling to room temperature. A cleaned zirconium surface is characterized with $R_o = 0.0$, $R_c = 0.0$, $R_p = 0.74$ and $R_{Zr} = 1.40$. 
5.3 Adsorption of PH₃ on the Zr(0001) Surface

5.3.1 Adsorption and Heating Effects

The prepared Zr(0001) surface was exposed to PH₃ at 2 x 10⁻⁷ Torr, and a measured uptake curve is shown in Figure 5.2. This curve indicates the phosphorus concentration on the surface increases almost linearly with PH₃ exposure, at least until the Rₚ value is around 3. In fact this study showed that the Rₚ value could reach 10 prior to the surface saturation. Similar to the situation with carbon adsorption on Zr(0001), heating will cause phosphorus to deplete from the surface, although we had no capability to investigate further whether this process involves bulk diffusion or desorption from the surface. The depletion curves (in Figure 5.3) were done with various initial phosphorus coverages followed by heating to increasing temperatures. From the curves one can see that the higher the initial Rₚ value, the lower the depletion temperature (here the depletion temperature is defined arbitrarily as the temperature at which the Rₚ value was reduced to 80% of its initial value). This could be due to increased repulsive interactions at the higher coverages. Alternatively it may be associated with partial physisorption in addition to chemisorption at the higher phosphorus coverages; the physisorbed phosphorus would be expected to deplete at lower temperatures than the chemisorbed phosphorus.
Figure 5.2 Auger peak height ratio $R_p$ plotted as a function of time of PH$_3$ exposure at 2x10$^{-7}$ Torr.
Figure 5.3 Phosphorus depletion versus temperature curves for different initial $R_p$ values marked on the vertical axis.
5.3.2 LEED Pattern for PH₂ Adsorbed on Zr(0001)

After different doses of PH₂, such that Rₚ is less than 2, and heating to 460°C (at this temperature free hydrogen has probably desorbed from the surface [50]), (1x1) LEED patterns were observed. These patterns are not very sharp, although the measured I(E) curves (Figure 5.4) for the (1,1) beam show only small changes compared with those from the clean zirconium surface. The high background in the LEED patterns appears to result from disordered phosphorus on the surface.

With higher doses of PH₂, so Rₚ exceeds 2, no extra features are seen in the LEED pattern on cooling to room temperature, after annealing at gradually increasing temperatures, until the heating temperature reaches 555°C. Then a faint (3x3) LEED pattern can be obtained, although this pattern is unstable in the presence of the electron beam (it exists for about 30 min.) and it is only measurable over a short energy range (around 60-120 eV). The latter is insufficient for a LEED crystallographic analysis. Figure 5.5 shows a LEED pattern from the Zr(0001)-(3x3)-P surface formed with an initial Rₚ value of 2.6, which reduces to 1.6 after annealing to 555°C. With this heating, some phosphorus depleted from the surface region and some of the rest formed the partially ordered (3x3) LEED pattern. No LEED patterns could be observed from surfaces with Rₚ values greater than 6.

The preliminary observation from LEED suggested that the heating temperature necessary to get the surface phosphorus coverage to order, and so form the (3x3) LEED pattern, also causes surface depletion. This is investigated further in the next section.
Figure 5.4 Comparison of experimental I(E) curves between the clean Zr(0001) surface and the (1x1)-PH$_3$ surface with different $R_p$ values when (a) $R_p = 1.18$ (b) $R_p = 1.38$ (c) $R_p = 1.49$. 
Figure 5.5 Picture of LEED pattern for Zr(0001)-(3x3)-PH$_3$ surface at 88 eV.
5.4 LEED Spot Profile Measurements

The LEED spot profile technique, in combination with AES, can be used to provide information about the surface ordering process. The specific interest is to identify the optimal ordering temperature and coverage for preparing a surface which shows a sharp (3x3) LEED pattern. A plot of the reciprocal of full width at half maximum (1/FWHM) for the intensity of the fractional beam (2/3,0) at 92 eV as a function of the final $R_p$ value is shown in Figure 5.6. After each exposure to PH$_3$, the sample was heated to 555°C and cooled to room temperature before measuring $R_p$ and 1/FWHM. Variation of the beam widths reflect variation in the size of the ordered regions that contribute to the (3x3) structure; specifically, larger values of 1/FWHM correspond to larger ordered regions [79]. Figure 5.6 shows that the optimal range for $R_p$ of the finally treated surface for forming (3x3) LEED patterns is from 1.3 to 1.6. In general these patterns are more diffuse than those other (3x3) patterns reported earlier by Wong et al with H$_2$S adsorption on the Zr(0001) surface [65].

Another approach to the type of information in Figure 5.6 is made by measuring 1/FWHM for the (2/3,0) beam at 92 eV and room temperature after heating to different higher temperatures. Information is shown in Figure 5.7(b) for an initial $R_p$ value equal to 2.5. Also shown in Figure 5.7(a) and Figure 5.7(c) are corresponding depletion curves associated with $R_p$ and $R_{Zr}$ respectively. The initial depletion in $R_p$ at around 100°C probably relates to some PH$_3$ desorption and the larger depletion in $R_p$
Figure 5.6 Variation for a Zr(0001)-(3x3)-P surface of normalized $1/\text{FWHM}$ for the $(2/3,0)$ beam at 92 eV as a function of phosphorus coverage resulting from increasing exposures to PH$_3$. 
Figure 5.7 (a) Normalized Auger peak-height ratio for phosphorus as a function of temperature. The Zr(0001) surface has been exposed to sufficient PH$_3$ to make the initial R$_0$ value at 2.5.
(b) Variation of normalized 1/FWHM for the (2/3,0) beam in the (3x3) LEED pattern at 92 eV for the same condition as in (a).
(c) Normalized Auger peak-height ratio R$^T_{Zr}/1.40$ as a function of temperature.
which starts at around 360°C may be associated with the desorption of another $\text{PH}_x$ species (or even free hydrogen). This is followed by a further phosphorus loss which starts at around 480°C. In principle the latter could involve either diffusion into the bulk or desorption from the surface. We did not have thermal desorption facilities to check which actually operates. However, a similar effect is not observed for sulphur below 600°C, which can provide a sharp (3x3) LEED pattern [65].

Figure 5.7(c) is the plot of $R_{Zr}^r$ versus temperature. Unlike the $R_{Zr}$ curve formed with the $\text{C}_2\text{H}_4$ adsorption (Figure 3.2), the $R_{Zr}^r$ curve here remains quite flat until the large surface phosphorus loss occurs, although a small kink at around 360°C may be associated with hydrogen desorption. Possibly this curve implies that the phosphorus (and even hydrogen) is less strongly bonded with zirconium in this particular case.

Figure 5.7(b) shows that the phosphorus ordering to give the (3x3) structure occurs especially in the temperature range from about 440°C to 560°C. Unfortunately though, in this temperature range the $R_p$ values show that there is also a significant loss of phosphorus. The latter may change the coverage sufficiently to prevent satisfying the condition to form ordered (3x3) domains according to the information in Figure 5.6. For example, when a $\text{PH}_3$-treated surface with an initial value of $R_p$ equal to 1.56 was gradually heated to 560°C, no third order features could be observed. In this case the $R_p$ value is reduced to 1.1, which indicates insufficient phosphorus to form a (3x3) LEED pattern. However, when the initial value of $R_p$ is 2.5, a (3x3) LEED pattern could be observed and the intensity of the (2/3,0) spot measured. For the second case, $R_p$ is reduced
to 1.6 after the annealing, but that value is apparently insufficient to form large and well-ordered (3x3) domains.

5.5 Final Comments

This thesis aims to add to our knowledge of the adsorption properties of the (0001) surface of zirconium. The combination of LEED and AES appears powerful for this purpose, although more detailed investigations would be helpful from other techniques including X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). The latter would be particularly important to follow the desorption of hydrogen from both adsorbed C\textsubscript{2}H\textsubscript{4} and PH\textsubscript{3} in this work. At present we can only assess the H loss indirectly from changes in Auger peak height ratios. Nevertheless the diffusion studies here for C at the Zr(0001) surface, when compared with previous studies for O and N, indicate that the effective diffusion temperatures decrease in the order C>N>O. This possibly implies, for a particular temperature, that O has a greater tendency to go to deeper layers than C, and that additionally may suggest that with dissociative underlayer adsorption of CO, the O is held below the C.

A detailed LEED crystallographic analysis would be helpful for the Zr(0001)-(1x1)-CO surface, and the present work provides some measurements to start such an analysis. The LEED analysis for the lower-coverage (1x1)-C structure follows those reported previously for the corresponding surfaces with N and O adsorption [51]; also this structure formed with
adsorbed C appears to match well with the known structure of bulk ZrC. This work provides a preliminary indication that the higher-coverage Zr(0001)-(1x1)-C structure may involve C adsorbed in tetrahedral holes. Although the structure of bulk ZrC$_2$ [80] is unknown, this proposed surface structure would contrast with that known for bulk ZrB$_2$ [73].

Throughout LEED structural work, there are discrepancies in intensity curves that may be due to neglected structural features, such as surface relaxations and disorder effects. Within LEED, as we currently do it, improved background subtraction techniques would be useful for obtaining better measured intensity curves. The spot profile analysis technique in LEED [81] can give information on defects, while scanning tunneling microscopy can provide complementary information in real space [20]. In this work, the disorder effects associated with the poorly developed (3x3)-PH$_3$ LEED pattern need to be better characterized. A recent development is indicating that diffuse LEED may be used to extract information about local bonding structure [82].
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