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ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION STUDIES OF SILICON AND TITANIUM OXIDE SURFACES

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ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION STUDIES OF SILICON AND TITANIUM OXIDE SURFACES

Yip-Wah Chung
(Ph. D. thesis)

July 1977

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

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ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION STUDIES OF SILICON AND TITANIUM OXIDE SURFACES

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ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION STUDIES
OF SILICON AND TITANIUM OXIDE SURFACES

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ABSTRACT

The work presented in this thesis is divided into two parts. The first part deals with chemisorption of acetylene, oxygen and aluminum on the silicon (111) surface as studied by Auger and electron energy loss spectroscopy and low energy electron diffraction. These studies suggest that the adsorption of acetylene on the silicon (111) - (7 x 7) surface takes place on preferred sites, due to the interaction of the silicon surface dangling bond orbitals and the \( \pi \) orbitals of the acetylene molecules. Electron energy loss spectroscopy studies indicate the possible splitting of the acetylene \( \pi \) orbitals when adsorbed onto the silicon (111) surface. Comparison of oxygen chemisorption on the silicon (111) - (7 x 7) surface and the same surface that is disordered by argon ion bombardment shows that oxygen is bound more strongly to the latter surface.

At a substrate temperature between 100 and 200°C, deposition of one monolayer of aluminum removes all intrinsic surface states of silicon and at the same time gives rise to new extrinsic interface electronic states. Low energy electron diffraction shows that the (7 x 7) pattern persists up to 0.5 monolayer of metal coverage. Further increase in aluminum coverage results in the loss of long range ordering. When the aluminum is deposited at a higher substrate temperature of
600-700°C, a well defined surface structure is obtained at one monolayer coverage and electron energy loss spectroscopy study shows the aggregation of aluminum atoms under these conditions.

In the second part, we concentrate on the study of titanium oxide and strontium titanate surfaces. The clean TiO$_2$(110) surface is unreconstructed while the (100) surface reconstructs to give (1 x 3), (1 x 5) and (1 x 7) surface structures when annealed at 500, 800 and 1200°C respectively. There is an accompanying decrease in the surface oxygen concentration with increasing annealing temperature. Prolonged argon ion bombardment removes oxygen preferentially and results in a surface composition close to Ti$_2$O$_3$, as shown by Auger measurements. The presence of surface Ti$^{3+}$ species is also indicated by the appearance of an emission peak at 0.6 eV below the Fermi level in UV photoemission and a 1.6 eV transition in the corresponding energy loss spectrum. Surface band-bending decreases by almost 1 eV in going from an oxygen-rich to a Ti$^{3+}$-rich titanium oxide surface. The oxygen-rich surface appears to be more inert and water is adsorbed associatively. On the other hand, water is decomposed into hydroxyl groups and hydrogen when adsorbed onto a Ti$^{3+}$-rich titanium oxide surface, generated either by argon ion bombardment or high temperature annealing.

While UV light illumination causes the Ti$^{3+}$ concentration on the TiO$_2$(100) - (1 x 3) surface to increase, there appears no observable change in the chemical nature of the adsorbed water. However, uv illumination on water adsorbed strontium titanate powder surfaces results in the evolution of hydrogen and oxygen, as a result of the photodecomposition of water. Based on the experimental information
on titanium oxide and the similarity between titanium oxide and strontium titanate, a mechanism is proposed to explain this photodecomposition process.
1. INTRODUCTION

In recent years there has been an exponential growth in surface related studies. This arises as a result of two closely related reasons:

(1) There is a need to understand processes occurring on solid surfaces in many important branches of science. For example, in the semiconductor technology in which devices are made smaller and smaller, one is faced with the problem of an increasing surface-to-volume ratio and thus non-trivial surface effects. In heterogeneous catalysis studies, one needs to understand how reactants adsorb on the surface of the catalyst, react through a series of intermediates to form the products which finally desorb from the catalyst surface. In materials science studies, one is confronted with the problem of how impurities segregate to the defects and grain boundaries and how these impurities affect the mechanical properties of materials.

(2) Ultra-high vacuum, i.e., pressures in the range of $10^{-9}$ torr or below, can now be achieved routinely so that well characterized surfaces can be produced and maintained so for a sufficiently long time for experimental investigations. Surface analytical tools such as low energy electron diffraction (LEED), Auger electron spectroscopy (AES), photoelectron spectroscopy (UPS and XPS) and energy loss spectroscopy (ELS) are available for the study of surface structure, composition, electron states and surface vibrations, thereby yielding information on surfaces that are not available previously.

In this study, investigations are made on the properties of clean silicon and titanium oxide surfaces, and their interactions with simple adsorbates. As is well known, silicon is technologically very important:
it is the basis of most of our semiconductor technology. Current development in the MOS (metal-oxide-semiconductor) device technology clearly requires a basic understanding of the oxidation of the silicon surface.\textsuperscript{1} This field was explored recently by Rowe and Ibach,\textsuperscript{2-4} using a number of surface analytical techniques, viz. Auger electron spectroscopy, electron energy loss and photoelectron spectroscopies. We have followed up on this work by comparing the difference in the oxidation characteristics between ordered and disordered silicon surfaces. This is then compared with the chemisorption characteristics of an electron donor, viz. acetylene on the same surfaces. Further, we have initiated the study of the deposition of controlled amounts of aluminum onto the silicon (111) surface and monitored the changes in the interface electronic states in the initial formation of such a metal-semiconductor contact. This provides information of great importance in any Schottky barrier type of devices, such as solar cells.

Our work on titanium oxide surfaces was initiated by some recent findings\textsuperscript{5-7} of the photochemical activity of this material. When titanium dioxide (as well as a number of other semiconductors, e.g., strontium titanate, ferric oxide etc.), was immersed into an electrolyte with a counter platinum electrode, an external voltage of only 0.25 volt is needed to electrolyze water into hydrogen and oxygen in the presence of light illumination of energy greater than the band gap of titanium dioxide (3 eV). In the case of strontium titanate, no external voltage is required. Normally, without light illumination, a voltage of at least 1.23 volts is required to decompose water. This so called photoelectrolysis process constitutes an example of
a broad and extremely interesting class of thermodynamically uphill reactions, and clearly shows great promise in the conversion of light into stored chemical energy. This has prompted us to undertake a comprehensive study of the properties of titanium oxide surfaces, with the hope of being able to understand the basic mechanism and do the photodecomposition reaction on a "half-cell" basis.

While the surface properties of silicon are well known, titanium oxide surfaces have rarely been explored. Various surface techniques were thus employed for such studies, the principles of which are discussed in Chapter 2. Chapter 3 gives an item-by-item description of the multiple surface technique experimental system. The interactions of oxygen, acetylene and aluminum with the silicon (111) surface are reported in Chapter 4. The work on titanium oxide surfaces will be described in three separate chapters. Chapter 5 describes the properties of clean titanium dioxide surfaces of different crystallographic orientations. Chemisorption studies of water on titanium oxide surfaces of different surface structures and stoichiometries are reported in Chapter 6. Chapter 7, the final chapter, gives an account of the preliminary work done on the effect of band gap radiation on water chemisorbed on titanium oxide and other related semiconductor surfaces.
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2. PRINCIPLES OF SURFACE ANALYSIS

In surface studies, one is confronted with the difficulty of detecting a small number of surface atoms in the presence of a large number of bulk atoms: a typical solid surface has \(-10^{15}\) atoms/cm\(^2\) as compared with \(-10^{23}\) atoms/cm\(^3\) in the bulk. In order to be able to probe the properties of solid surfaces using conventional methods, one needs the use of powders with very high surface-to-volume ratio so that surface effects become dominant. However, this technique suffers from the distinct disadvantage of an entirely uncontrolled surface structure, which is known to play an important role in surface chemical reactions.\(^1\) It is thus desirable to use specimens of well defined surface structures and examine them with tools that are surface sensitive. It turns out that electrons with energies in the range of 10 to 1000 eV are ideally suited for this purpose. Figure 2.1 shows a plot of the mean free paths of electrons in solids vs their energies. The curve exhibits a broad minimum in the energy range between 10 and 1000 eV, with the corresponding mean free path on the order of 4 to 20\(\AA\). Electron emission from solids with energy in this range must therefore originate from the top few atomic layers. Experimental techniques involving the excitation and detection of electrons having energy between 10 and 1000 eV are thus surface-sensitive.


Suppose we collimate a monoenergetic beam of electrons, energy \(E_p\) and allow it to hit a solid surface. A typical plot of the number of scattered electrons \(N(E)\) as a function of their kinetic energy \(E\) is shown in Fig. 2.2. The \(N(E)\) vs \(E\) curve is usually dominated
Fig. 2.1. A plot of the mean free path of electrons vs electron energy for various solids. Note the minimum around 100 ev.
Fig. 2.2. A typical plot of the energy distribution of electrons scattered from a solid surface when a monoenergetic beam of electrons, energy $E_p$, impinges on the surface.
by a strong peak at low energies, due to secondary electrons, created as a result of inelastic collisions between the incident electrons and electrons bound to the solid. The rest of the spectrum consists of three major features which turn out to be extremely useful in surface characterization:

2.1.1. The Elastic Peak

A portion of the incident electrons, typically a few percent, is scattered elastically from the surface without any observable energy loss. For electrons with primary energies of 10 to 200 eV, their de Broglie wavelength are comparable to the atomic spacings on the surface and are thus capable of producing a diffraction pattern characteristic of the surface unit cell. By measuring the intensity of each diffraction spot, one can, in principle, determine the position of each atom in the surface unit cell. This technique is known as low energy electron diffraction (LEED).

2.1.2. Energy Loss Peaks

These are caused by energy loss of the incident electrons in exciting interband electronic transitions. The hypothetical case for a two-level system is illustrated in Fig. 2.3, in which there are two electronic levels at energy Δ apart, with the lower level occupied and upper level empty (Fig. 2.3(a)). The energy loss spectrum obtained from this system with a monoenergetic electron beam and measuring the resulting electron energy distribution is depicted in Fig. 2.3(b). The elastic peak is shown as one with zero energy loss and the loss peak is found at an energy Δ below it. In real solids, the loss spectrum is not so simple because of much more complicated electronic levels.
Fig. 2.3. (a) A simple two-level system. (b) Energy loss spectrum from this two-level system.
In addition to these interband electronic transitions, there are also electron energy losses due to surface vibrations. The energy loss involved is much smaller, viz -100 meV, as compared with interband excitation -eV. To be able to observe these surface vibrations, we require the use of highly monoenergetic electrons, typically with energy spread < 10 meV. This is one of the few techniques capable of detecting hydrogen on metal or semiconductor surfaces and has tremendous potential of developing into a major technique in the study of bonding on surfaces.4,5

2.1.3. Auger Electron Emission

The basic mechanism of this process is illustrated in Fig. 2.4 for a KLILIII transition. When an incident electron has kinetic energy greater than the binding energy of the K-shell electron of an atomic species, there is a non-zero probability that the atom will be ionized by losing a K-shell electron. An electron from the LI shell fills this vacancy. The excess energy $E_K - E_{LI}$ can then be released as a photon (as in X-ray fluorescence) or given to an electron in the LIII shell, which then leaves the atom with energy $E_K - E_{LI} - E_{LIII}$, characteristic of the parent atom. This is known as an Auger electron. By measuring the energy of the ejected Auger electron, one can therefore determine the chemical composition of the surface. Moreover, changes in the Auger peak shape and energy position can sometimes be observed as a result of changes in the oxidation state of the atomic species.6
Fig. 2.4. An illustration of the $KL_1L_{III}$ Auger electron emission process.
2.2. **Photoelectron Spectroscopy**

To study the occupied density of states in solids, which includes the valence bands and the core levels, one makes use of the photoelectric effect whereby electrons in the solid are excited into the vacuum by means of photons and are analyzed as a function of their kinetic energies (Fig. 2.5). The photoelectron energy distribution $N(E, \nu)$ is given by the well-known golden rule:

$$N(E, \nu) = \int_{BZ} d^3k \sum_{i,f} |t_{fi}(\vec{k})|^2 \delta(\vec{k}_f - \vec{k} - \vec{k}_\nu - \vec{G})$$

$$\times \delta(E_f(\vec{k}_f) - E_i(\vec{k}) - \nu) \delta(E - E_i(\vec{k}))$$

where $t_{fi}$ is the transition matrix element between an initial state of wavevector $\vec{k}$ and energy $E_i(\vec{k})$ and final state of wavevector $\vec{k}_f$ and energy $E_f(\vec{k}_f)$; $\delta$ functions guarantee energy and momentum conservation; $\vec{k}_\nu$ is the photon wave vector; $\nu$ the photon energy; and $\vec{G}$ reciprocal lattice vector. Assuming constant transition matrix elements,

$$N(E, \nu) = \sum_{i,f} \int_{BZ} d^3k \delta(\vec{k}_f - \vec{k} - \vec{k}_\nu - \vec{G}) \delta(E_f - E_i - \nu) \delta(E - E_i)$$

$$- \sum_{i,f} J_{fi}(\nu) \delta(\vec{k}_f - \vec{k} - \vec{k}_\nu - \vec{G}) \delta(E - E_i)$$

where

$$J_{fi}(\nu) = \int_{BZ} d^3k \delta(E_f - E_i - \nu)$$

is the joint density of states. By further assuming that states
Fig. 2.5. Illustration of the photoelectric effect. Final state and matrix element effects are not depicted here.
throughout the first Brillouin Zone contribute to the photoemission spectrum, as can be achieved by using a large angle electron detector, the photoelectron energy distribution will then be proportional to the joint density of states $J_{\mathbf{f}_1}(h\nu)$, which, at sufficiently large photon energy, approximates very closely the occupied density of states.\textsuperscript{7}

When this technique was first developed by Siegbahn, et al.\textsuperscript{8} in the 1960's, photoelectron spectroscopy was used as a finger-painting technique. But now, photoemission has developed into a sophisticated technique by means of which initial state symmetry,\textsuperscript{9} orientation and bonding of adsorbed molecules\textsuperscript{10} on metal surfaces can be determined. With the advent of tunable and polarized synchrotron radiation, photoemission will undoubtedly find applications in other important areas of physics and chemistry.
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3. THE MULTIPLE TECHNIQUE EXPERIMENTAL SYSTEM

3.1. Introduction

The experiments were all performed inside an ion-pumped stainless steel ultra-high vacuum system. The ion pump has a rated pumping speed of 1600 litres per second, and is separated from the experimental chamber by a poppet valve. A 12-hr bake at 150°C is usually sufficient to bring the system pressure down to $1 \times 10^{-10}$ torr or less, as monitored by a Bayard-Alpert ionization gauge located close to the poppet valve.

The instruments attached to the system can be divided into three categories: (1) specimen manipulation and cleaning, which includes the manipulator, specimen holder, gas inlet manifold and ion bombardment facilities; (2) residual gas analysis, which includes a quadrupole mass spectrometer; (3) surface analysis, which includes LEED optics, a double-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun, and a He I photon (energy being 21.2 eV) generator, capable of doing LEED, AES, EELS and UPS sequentially on the same specimen. A schematic layout is shown in Fig. 3.1, various parts of which are described in the following sections.

3.2. Specimen Manipulation and Cleaning

3.2.1. Specimen Manipulator and Holder

The specimen manipulator (PHI model 10-504) is capable of translations in the x, y and z directions, tilting of the specimen stage and a 360° rotation about the axis of the manipulator. In most studies the specimen was mounted on a high density alumina holder, with a tungsten or tantalum wire heater mounted at the back of the crystal. The heater wire was wound non-inductively to minimize the
Fig. 3.1. The multiple surface technique experimental system.
magnetic field generated by the heater current. In this way, both Auger and energy loss spectra can be obtained during heating of the specimen. The specimen must be electrically shorted to the specimen stage to avoid charging.

3.2.2. Ion Bombardment

For in-situ specimen cleaning, argon gas was introduced from an inlet manifold into the system through a leak valve to a pressure of 5-8 x 10^-5 torr. The same inlet manifold was used for introducing other gases for chemisorption studies. An ion bombardment gun (Varian model No. 981-2043) with deflection plates to maneuver the ion beam, was employed for sputtering. Typical sputtering conditions were: ion energy = 2 keV, ion beam current 10 microamps, beam diameter ~1.0 cm. During sputtering, the ion pump was isolated from the experimental chamber and a titanium sublimation pump was used for pumping residual active gases outgassing from the walls of the chamber.

3.3. Residual Gas Analysis

An EAI quadrupole mass spectrometer was used to monitor the residual gas composition and perform thermal desorption measurements. Under the most severe conditions of noise interference (e.g., from nearby mechanical pumps), pressure changes on the order of 10^-12 torr are readily detectable. For a system pumping speed of 10 litres per sec, this corresponds to a particle number change of 3.2 x 10^8 per sec, which is more than sufficient for most flash desorption experiments.
3.4. Surface Analysis

3.4.1. The Cylindrical Mirror Analyzer (CMA)

The heart of this surface analytical system is the PHI 15-25G double-pass cylindrical mirror analyzer with an internal coaxial electron gun. This is used as a primary electron source for Auger and electron energy loss studies, and as an energy analyzer for obtaining Auger, electron loss and photoelectron energy distributions. A detailed description of its operation principle has been given by Sar-El.\(^1\)

The CMA is superior to the retarding field grid analyzer (RFA) in having very low shot noise which allows a faster energy analysis, or the use of smaller beam currents to minimize electron beam damage on surfaces.\(^2\) Moreover, because of its second order focusing properties, the CMA has a very high transmission for a given energy resolution, \(-10\%\) for single-pass CMA and \(-6\%\) for double-pass CMA with energy resolution \(\leq 0.7\%\).\(^3\)

The energy resolution of the PHI 15-25G double-pass CMA was measured to be 0.007. That is, given a monoenergetic beam of electrons, energy \(E_p\), the output signal from the CMA will have a full energy width at half maximum of 0.007 \(E_p\). Therefore, for better absolute energy resolution, it is necessary to operate the analyzer in the retard mode, i.e., the incoming electrons are retarded to a certain set pass energy before the energy analysis is performed. For example, at a set pass energy of 50 eV, the energy resolution would be 0.35 eV. The signal intensity is inversely proportional to the pass energy because of an accompanying decrease in the effective source size.
3.4.2. Auger Electron Spectroscopy (AES)

In order to perform Auger analysis, the specimen must first be positioned at the focal point of the CMA. This can be achieved by translating the specimen along the axis of the CMA to maximize the elastic peak. Usually the specimen was positioned with the primary electron beam at normal incidence. Typical beam voltages were 1.5 to 2 keV. The Auger spectrum was usually obtained in the first derivative mode by modulating the voltage on the outer cylinder at a frequency $\omega$ and detecting the signal at the same frequency by means of a lock-in amplifier. In most of the work described here, the analyzer was operated in the retard mode to give an energy resolution of approximately 1.5 eV.

3.4.3. Electron Energy Loss Spectroscopy (ELS)

Essentially, the same arrangements and electronics were used for energy loss measurements. The primary beam energies were in the range of 50 to 200 eV in order to achieve maximum surface sensitivities. The scattered electrons were analyzed at an angle of $42.3^\circ \pm 6^\circ$ from the axis of the CMA over all azimuth angles. The analyzer was operated in the retard mode at a pass energy of 50 eV. Theoretically, this should give us an energy resolution of 0.35 eV. However, since no primary beam energy selection was performed, the ultimate resolution was limited by the thermal spread of the incident electrons, which was about 0.6 eV. The spectral features were enhanced by taking the negative of the second derivative of the electron energy distribution as a function of energy loss. This was achieved by modulating the
pass energy at a frequency and detecting the signal at a frequency of $2\omega$.

3.4.4. Ultraviolet Photoelectron Spectroscopy (UPS)

In all our photoemission studies, the He I spectral line at 21.2 eV was used for photo-excitation. This was obtained by a d.c. cold cathode discharge of helium at approximately 1 torr. Since there exists no suitable window material for light of energy greater than 12 eV (cutoff energy of lithium fluoride), a windowless operation must be employed.

The pressure was dropped sequentially by means of two stages of differential pumping from 1 torr in the discharge capillary, to 0.1 torr in the first stage, then to $1-2 \times 10^{-5}$ torr in the second stage and finally to $1-2 \times 10^{-9}$ torr in the experimental chamber, which could be isolated from the differential pumping manifold by means of a valve mechanism.

In gas adsorption studies, this isolation valve was closed to avoid backstreaming of the introduced gas into the discharge lamp and generating impurity spectral lines. It should be noted that the pressure rise during UPS operation was mainly due to an inflow of helium into the chamber and posed no contamination problems to surfaces under investigation.

A schematic diagram of this He I photon generator is shown in Fig. 3.2.

The angle of incidence of the photons was $75^\circ$ from the axis of the CMA.

A port aligner on the differential pumping manifold was used for maneuvering the light beam to maximize the photoelectron signal.

Because of the low kinetic energy of the emitted photoelectrons (approximately 0 to 17 eV), very small residual magnetic field may affect the photoelectron trajectory into the CMA significantly. The position of the specimen was periodically checked by directing a
Fig. 3.2. HE(I) PHOTON GENERATOR

A. 9 CM LONG, 5 MM I.D.
B. 2 " , 1.5 "
C. 7 " , 1.5 "
D. 13 " , 1 "

---

XBL 776-8906
10 eV electron beam towards the specimen and moving the specimen to maximize the elastic peak. To allow the slowest photoelectrons to be collected by the CMA, a small negative (~3-6 volts) bias was applied to the specimen in all photoemission experiments.

In a typical operation, the discharge current was 150 mA and the power dissipated by the lamp was 65 watts. The photoelectron signal detection system is illustrated in Fig. 3.3. Single electron pulses are produced by photoelectrons hitting the channeltron electron multiplier. The pulses are then amplified, shaped before feeding into the discriminator. The photoelectron counts are then stored in a multichannel scaler, which can store up to 4 spectra and perform addition and subtraction on each individual spectrum. Usually, a spectrum can be obtained in 5 min with a signal-to-noise ratio better than 70 to 1.

3.4.5. Low Energy Electron Diffraction (LEED)

The system was equipped with PHI 15-120 LEED optics, a conventional 4-grid retarding field analyzer. The LEED screen was coated with a green phosphor, making observation by eye relatively easy, as compared with a blue phosphor. In most studies such as energy loss and photoelectron spectroscopies, it was a general practice to keep the distance of the specimen from the axis of the manipulator constant once it was optimized. When the specimen was rotated in front of the LEED optics, this distance was such that the specimen was always slightly offset from the centre of curvature of the electron optics. The LEED pattern was then slightly distorted. This problem was considered tolerable as long as the symmetry of the spot pattern was discernible.
Fig. 3.3. The pulse counting electronics system for UPS studies.
REFERENCES

3. These are specifications given by Varian Associates and Physical Electronics Industries.
4. Suppose the modulation is of the form $E_M \cos \omega t$. Then the scattered electron distribution $N(E + E_M \cos \omega t)$ can be expanded in Taylor series, viz

$$N(E + E_M \cos \omega t) = N(E) + E_M \cos \omega t \frac{dN}{dE} + \frac{1}{2} E_M^2 \cos^2 \omega t \frac{d^2N}{dE^2} + \ldots$$

assuming that $E_M \ll E$. The first term is a d.c. current and can be neglected in a.c. measurements. Clearly detecting the $\omega$ term gives the first derivative of $N$ as a function of $E$. Now look at the third term.

$$\cos^2 \omega t = \frac{1}{2} (1 + \cos 2\omega t)$$

i.e.,

$$\frac{1}{2} E_M^2 \cos^2 \omega t \frac{d^2N}{dE^2} = \frac{E_M^2}{4(1 + \cos 2\omega t)} \frac{d^2N}{dE^2}$$

Therefore, the second derivative of the electron distribution as a function of energy can be obtained by detecting the $2\omega$ term.
4. THE SILICON (111) SURFACE

I. CHEMISORPTION OF OXYGEN AND ACETYLENE

II. DEPOSITION OF ALUMINUM

Silicon is among one of the materials whose surface properties have been heavily explored, both experimentally and theoretically, on account of its technological importance. In Section 4.1, we will review over the structural and electronic properties of the silicon (111) surface, as the majority of the data were on this surface. This arises from the fact that the (111) surface is the cleavage plane of silicon and most clean surfaces are obtained by cleavage. However, recently, there is a surge of interest in the study of the silicon (100) surface, primarily because it exhibits the negative electron affinity effect, which has potential applications as efficient photodetectors.

After this, results of an energy loss study of the chemisorption of oxygen and acetylene on the silicon (111) surface will be presented in Section 4.2. This constitutes the first energy loss study of organic molecules adsorbed on silicon surfaces. There are marked structure-dependent differences in the ELS spectra in the presence of these adsorbates. A model of acetylene orientation on the silicon (111) surface is proposed to explain the experimental results. The ELS data suggest that the electrons in the Si-O chemisorption bond are more tightly bound on the disordered surface than the silicon (111) surface with a (7 x 7) surface structure.

Electron energy loss spectroscopy and LEED have been used to study the formation of Schottky barrier on the silicon (111) surface with evaporated aluminum at different substrate temperatures ($T_s$). Aluminum deposition at a substrate temperature of 100-200°C results in the disappearance of electronic surface states on silicon (111) - (7 x 7) surface. It is further demonstrated that aggregation of aluminum atoms occurs on the silicon surface after the deposition of either 2 monolayers of aluminum at $T_s = 100-200$°C or one monolayer of aluminum at $T_s = 600-700$°C. These results will be presented and discussed in Section 4.3. Suggestions for further research are described in Section 4.4.

4.1. Review of the Properties of Clean Silicon (111) Surfaces

4.1.1. Structural Properties

According to numerous LEED studies,\textsuperscript{2-4} the structure of the silicon (111) surface depends on the preparation and thermal history. If a silicon (111) surface is produced by cleavage at room temperature, a (2 x 1) structure is obtained, i.e., one of the unit vectors on the surface is twice that projected from the bulk, whereas the other surface unit vector remains unchanged. Annealing at about 300°C gives the (1 x 1) structure and further heating to 600°C results in the (7 x 7) structure. This phenomenon is known as reconstruction, which is caused by the movement of atoms in the top few atomic layers away from ideal lattice positions. The aforementioned transformations are irreversible.\textsuperscript{4} However, reversible transition from the (7 x 7) to the (1 x 1) structure at about 900°C has been observed.\textsuperscript{5}
The most notable explanations for silicon surface reconstructions are those of Haneman\textsuperscript{6} and Lander and Morrison\textsuperscript{2}. Both models give mechanisms to explain changes in the length of the unit vectors on the surface during reconstruction. For the (2 x 1) structure, Lander and Morrison presumed that surface atoms of alternating rows are displaced laterally and form double bonds with those not displaced, thereby giving rise to the (2 x 1) unit cell. On the other hand, Haneman\textsuperscript{6} proposed a "buckled" model in which he argued that the usual sp\textsuperscript{3} tetrahedral bonding (bond angle about 109°) in the bulk must be different on the surface because of the sudden change in the potential. Since each surface atom is bonded to three atoms in the second layer, with one "dangling" orbital normal to the surface, then if this dangling bond is allowed to become more p-like, the remaining three bonds will become more sp\textsuperscript{2}-like, with bond angle approaching 120°, so that the surface atom concerned will be lowered. The resultant lateral stress is relaxed by the raising of alternate surface atoms, in which case the dangling bond becomes more s-like, while the other three bonds become more p-like. This then also gives rise to the (2 x 1) surface structure. On the basis of surface energy calculation,\textsuperscript{7} spin resonance\textsuperscript{8} and mating characteristics,\textsuperscript{9} the Haneman model appears to be a satisfactory explanation for the (2 x 1) structure.

For the (7 x 7) structure, Lander and Morrison\textsuperscript{2} proposed that some atoms (about 25\%) are removed from their normal lattice sites and the surface atoms form double bonds with atoms of the second layer. On the other hand, no model similar to Haneman's has been offered for the (7 x 7) structure. An analogous model that the seventh atom
along every seventh row is displaced relative to the surface can be considered. However, it is not immediately obvious why such a transition requires thermal activation. The surface vacancy model, on the other hand, involves the migration of surface atoms and thus requires thermal energy. It is also consistent with the fact that the (7 x 7) lattice is stable below 700°C once it is formed, because of low surface migration rate of silicon atoms at these temperatures. Recent experimental results on work function and UPS studies\textsuperscript{10} seem to favor the vacancy model for the (7 x 7) structure. However, it is found that while the energy to form a vacancy on a silicon (111) surface is very large, silicon atoms outside the normal surface (add-atoms) should be quite stable. Based on this consideration, Harrison\textsuperscript{11} suggested that the (7 x 7) reconstruction is a pattern of add-atoms rather than (and topologically unrelated to) a pattern of vacancies.

Perhaps the only conclusive way of determining the structure of the silicon surface unit cell is by low energy electron diffraction in which experimental intensity vs electron energy curves are compared with dynamical LEED calculations, assuming different unit cell geometries. The complexities involved, especially with the silicon (111) - (7 x 7) surface, discourage any such attempts. Recent developments in extended X-ray absorption fine structure\textsuperscript{12} (EXAFS) appear to offer some hope of elucidating surface structure in a simpler way.

4.1.2. Electronic Properties

4.1.2.1. Experimental Results. Perhaps the first definite experimental proof for the existence of surface states in silicon is that of Allen and Gobeli,\textsuperscript{13} in which the Fermi level at the surface
was determined over the entire available range of bulk doping for atomically clean silicon (111) surfaces cleaved in ultra-high vacuum at room temperatures. A "pinning" effect was observed, i.e., the Fermi level stays almost constant relative to the vacuum level, irrespective of bulk doping from $10^{18}$ cm$^{-3}$ p-type to $10^{18}$ cm$^{-3}$ n-type. This can be explained by the dangling bond model, in which each broken bond on the cleaved surface gives rise to two surface associated states, one of which must be filled for a neutral surface. On an n-type semiconductor surface, a few of the normally empty states will be filled, causing a net negative surface charge, which is compensated by ionized donors inside the semiconductor, and a subsequent upward hand-bending (Fig. 4.1(a)). An analogous situation for a p-type semiconductor is depicted in Fig. 4.1(b).

In the same experiment, Allen and Gobeli$^{13}$ estimated a surface state density on the order of $10^{15}$ cm$^{-2}$ (~ surface atom density) and they found that a two-band model would fit their data satisfactorily. This finding is further substantiated by an optical absorption experiment$^{14}$ in which the authors showed that the existence of two surface state bands in the band gap, each about 0.1 eV wide, separated by approximately 0.3 eV, is necessary to explain their data. High resolution energy loss spectroscopy study on the (2 x 1) surface$^{15}$ also supports this two-band model.

In addition, photoemission studies on the (2 x 1) surface$^{16,17}$ showed that there is an approximately 1 eV wide occupied surface state band centred at about 0.45 eV below the silicon valence band maximum. The observation that the energy position of the surface state emission
Fig. 4.1. Typical energy band diagrams for (a) n-type and (b) p-type semiconductors in contact with vacuum.
is essentially independent of photon energy over the range of 10 to 20 eV while that of the bulk emission changes markedly shows that surface state and bulk emission are due to indirect and direct optical excitation respectively. This is expected because of the localization of the surface states. Angle-resolved photoemission measurements demonstrated that photoelectron emission from these surface states is very anisotropic and is related to the surface symmetry.\(^1\) Cleaved silicon surfaces with high step densities give rise to extra surface states just below the Fermi level.\(^{19}\)

Annealing the (2 x 1) surface at 600°C results in the formation of the (7 x 7) surface structure, which exhibits striking difference in electronic surface state distributions. It was found by both optical absorption\(^{20}\) and energy loss spectroscopy\(^{15}\) that the strong transition at 0.5 eV that exists on the (2 x 1) surface disappears on the (7 x 7) surface. Photoemission measurements on the (7 x 7) surface showed a metallic edge at the Fermi level.\(^{21}\) Furthermore, by comparing the photoemission spectra of silicon (100) and (111) surfaces of different surface structures, one can infer that surface states exist throughout the band gap and the whole 12-eV wide valence band.\(^{21}\)

4.1.2.2. Theoretical Survey. Various techniques used in the calculation of surface states before and after 1970 are described in detail in the review papers by Davison and Levine, and Appelbaum and Hamann.\(^{22}\) A summary of the analyses and results on silicon is given below.

Koutecky and Tomasek\(^{23}\) assumed that the bulk can be represented by a tight binding scheme and the (111) surface is terminated by
removing atoms. Their most important finding is the existence of a merged band of surface states in the band gap. More elaborate calculations by Pugh24 showed essentially the same behavior, except for a slightly different position of the surface band relative to the midgap. Jones25 carried out a pseudopotential calculation of the ideal (110) surface of silicon and constructed an E - k diagram for the surface state band. He found a continuous band of surface states across the band gap and many of the states are located outside it. This is one of the first theoretical calculations which indicate the extent of surface effects outside the band gap. By using a similar formalism, Yndurain and Elices26 reached the same conclusion for the silicon (100) and (111) surfaces.

So, up to this point, the existence of surface states appears well established theoretically, although there is disagreement as to the location and extent of the surface bands. However, effects of surface relaxation and reconstruction were not taken into account in all the above theoretical treatments. Moreover, the relationship between the semiclassical "dangling bond" concept and the quantum mechanical results of surface states in the band gap was not established quantitatively by these theories.

Instead of using an abrupt unphysical potential in the surface region, Appelbaum and Hamann27 constructed a surface potential for silicon by adjusting it to fit the experimental value of electron affinity. The analysis was made on the silicon (111) - (1 x 1) surface with and without lattice relaxation. For the unrelaxed structure, they found a band of surface states lying between 0.03 and 0.61 eV
above the valence band maximum. The electron density for this band has a large lobe at the cleavage plane, zero at the surface atom and a secondary lobe behind it. This feature characterizes a dangling bond. For the relaxed structure, three surface bands were found: (1) dangling bond states in the gap, with a more p-like character, because of the inward relaxation of the surface atom; (2) back-bonding state between -2 and -3.6 eV with respect to the valence band maximum, due to charge localization between the first and the second planes of surface atoms; (3) bonding state between -11 and -13 eV, due to broad charge distribution along bonds between the first and second, as well as the second and the third planes of atoms. This result provides a satisfactory explanation for the ELS results reported by Rowe and Ibach. A semi-empirical calculation for the relaxed silicon (111) - (1 x 1) surface gave essentially the same results. By employing a self-consistent calculation, Appelbaum and Hamann were able to give the variation of potential and charge density near the surface, enabling one to see a picture of the "real" silicon-vacuum interface.

Recently, the self-consistent pseudopotential technique was applied to the electronic state calculation of silicon (111) surfaces. Three different surface models were studied: (1) unrelaxed (1 x 1) surface, (2) relaxed (1 x 1) surface and (3) relaxed (2 x 1) surface, based on the Haneman model. In addition to the features given by Appelbaum and Hamann for the first two structure, this calculation gives a most important result. For the (1 x 1) structure, there is only a broad band of surface states extending throughout the gap.
This changes entirely for the (2 x 1) structure. Enlarging the real space unit cell in one dimension corresponds to folding back the Brillouin zone in a certain direction. Therefore, two split bands appear as a result of this reconstruction, the lower (upper) band corresponding to electrons localizing in the raised (lowered) atoms. The two peaks thus allow an optical transition, as observed by Chiarotti, et al.\textsuperscript{14} and Rowe, et al.\textsuperscript{15} Moreover, the lower band is located very close to the valence band edge and is probably the surface state observed in photoemission.\textsuperscript{16,17} Calculations by the scattered-wave cluster model\textsuperscript{32} and the tight-binding method\textsuperscript{33,34} yield similar conclusions about the nature of these split bands. The same pseudo-potential method has been applied to study a silicon (111) step surface model.\textsuperscript{35} The dangling bond surface states are strongly affected by the presence of steps. New states are found to give rise to additional structures in the density of states, which agrees well with photoemission results.\textsuperscript{19}

4.2. \textit{Electron Energy Loss Spectroscopy Study of the Chemisorption of Oxygen and Acetylene}

4.2.1. \textit{Specimen Preparation and Special Techniques}

The specimen used throughout the experiments was a 2500 ohm-cm p-type silicon single crystal of (111) orientation, mechanically polished with 0.05 micron diameter Al\textsubscript{2}O\textsubscript{3} powders, and etched in a 1:1 mixture of concentrated HF and HNO\textsubscript{3} acids to remove any gross contaminants left on the surface. This was then rinsed thoroughly in ethanol and mounted in a high density alumina holder with a tungsten or tantalum heater at the back of the crystal. The major surface contaminants after bake-out were carbon and oxygen, which could be removed by
sputtering with an argon ion beam of 2 keV and 10 µA at an argon pressure of 5 x 10^-5 torr. The surface is considered clean when the Auger peak ratio of O(510 eV) and C(272 eV) to Si(92 eV) drops below 0.1%. This argon-ion disordered surface could be subsequently annealed at 800°C for about 30 min to give the (7 x 7) surface, as detected by LEED (Fig. 4.2). Once this clean ordered surface is produced, background gas (mainly hydrogen and carbon monoxide) adsorbed on the silicon surface can be removed by heating to 600°C for approximately 1 min.

Oxygen (resp. acetylene) was introduced into the system through a leak valve, with the poppet valve between the ion pump and the experimental chamber closed. The dosage was determined from the pressure increase and the time of exposure. The partial pressure used was typically in the range of 10^-5 to 10^-7 torr. The coverage was determined by observing the ratio of oxygen (resp. carbon) Auger signal to that of silicon as a function of exposure. We will subsequently call the saturation coverage to be θ = 1, although this may correspond to different numbers of gas molecules adsorbed per unit surface area on the ordered and disordered surfaces, as discussed below.

4.2.2. Results and Discussion

4.2.2.1. The Clean Surfaces. The energy loss spectrum for the clean silicon (111) - (7 x 7) surface is shown in Fig. 4.3. This is identical to that of Rowe and Ibach,28 except that the E1 transition shows up more clearly here, probably as a result of better resolution. The peaks labelled E1 and E2 are attributed to bulk interband transition, which are close to those observed in optical absorption experiments. Bulk and surface plasmon losses are indicated by \( \hbar \omega_p \) and \( \hbar \omega_s \) respectively.
Fig. 4.2. LEED pattern obtained from the silicon (111) - (7 x 7) surface.
Fig. 4.3. Electron energy loss spectra obtained from clean silicon surfaces at an electron energy of about 100 eV: (a) the silicon (111) - (7 x 7) surface, and (b) the argon sputtered silicon (111) surface.
On account of its small transition energy, $S_1$ arises most likely from the dangling states, while $S_2$ and $S_3$ arise from backbonding states.\textsuperscript{27,28} The argon ion disordered silicon (111) surface, on the other hand, exhibits a number of differences in the ELS spectrum. The assigned bulk transitions $E_1$ and $E_2$ shift slightly, indicating that the "bulk" band structure changes noticeably in the topmost layers. The backbonding states $S_2$ and $S_3$ are found only as shallow shoulders on the disordered surface. A weak shoulder, not found previously, is located slightly above the surface plasmon peak. This peak disappears on annealing and/or prolonged exposure to ultra-high vacuum. This behavior suggests that it is a surface-related transition, and from its transition energy of 11.6 eV, this energy loss peak probably arises from backbonding state transitions.\textsuperscript{29} Observation of these surface transition is a strong evidence for the existence of surface states near the bandgap and in the whole valence band as well, as predicted in a number of theoretical calculations.\textsuperscript{27,29,31,32}

4.2.2.2. Effect of Acetylene Exposure on the Ordered and Disordered Silicon Surfaces. On the silicon (111)- (7 x 7) surface, exposure at room temperature to acetylene causes attenuation of peaks due to bulk and surface transitions, except for the $S_2$ transition which sharpens up and becomes stronger with increasing acetylene coverage (Fig. 4.4). The rate of attenuation of other surface-related peaks, viz $S_1$ and $S_3$, as a function of increasing exposure is small. In fact, after 2000 L (1 L = 10^{-6} torr-sec) of acetylene exposure, the $S_1$ transition still survives. Above $\theta = 0.5$, the $E_1$ transition at 3.2 eV is dominated by a growing acetylene-induced peak at 3.6 eV. Another peak at 8.4 eV
Fig. 4.4. Electron energy loss spectra of the silicon (111) - (7 x 7) surface with various coverages of acetylene.
shows up as a shoulder of the 7.3 eV transition. At saturation of the surface with adsorbed acetylene, LEED showed very weak one-seventh order spots and no new structures, indicating that acetylene does not form an ordered overlayer on the silicon (7 x 7) surface. Flashing the crystal produced an acetylene peak in the quadrupole mass spectrometer, indicating that most of the acetylene is not decomposed on the surface. This is the only case in silicon chemisorption studies in which the adsorbate causes the disappearance of the non-integral spots while maintaining the dangling state transition ($S_1^*$). This indicates that the (7 x 7) reconstruction is not due to the presence of dangling bonds. Ibach and Rowe$^{36}$ arrived at a similar conclusion in their study of hydrogen chemisorption on silicon surfaces.

A recent study of the surface crystallography of acetylene on the platinum single crystal surface of (111) orientation indicates that acetylene sits in a triangular site when it is adsorbed in the stable state.$^{37}$ The UPS studies,$^{38}$ as discussed in the Appendix, show that the $\pi$ orbitals in acetylene are split into two levels, separated by -1.5 eV, as a result of the adsorbate-substrate interaction. Let us assume a similar model for the adsorbed acetylene on the silicon (111) surface, with its $\pi$ orbitals overlapping with the silicon dangling bonds. The silicon crystal field will cause the splitting of the acetylene $\pi$ orbitals. Assuming that the $\pi$ electrons have the same final state in energy loss experiments, this would account for the two transitions at 7.3 and 8.4 eV. A splitting of 1.1 eV seems reasonable in comparison with the result of acetylene on the platinum (111) surface. By placing acetylene molecules randomly (as evidenced by LEED) on
Fig. 4.5. Electron energy loss spectra of the silicon (111) disordered surface with various acetylene coverages.
the ordered silicon surface in these triangular sites, there will still be silicon surface atoms not bonded to any acetylene molecules, which explains the incomplete removal of the $S_1$ transition. The incomplete coverage of all sites is also indicated by the observed small carbon to silicon Auger peak ratio on the ordered clean silicon surface (0.02), as compared to the corresponding ratio on the disordered surface after saturation (0.03).

This interpretation of bonding can be further tested by uv photoelectron spectroscopy, since the presence of split peaks due to the $\pi$ orbitals of acetylene and the variation of their relative intensities in the UPS spectrum as a function of the polar angle should be detectable.

4.2.2.3. Effect of Oxygen exposure on the Disordered Silicon Crystal Surface. Changes in the surface transitions on the disordered silicon crystal surface with increasing oxygen coverage are similar to that observed for the silicon (111) - (7 x 7) surface,\textsuperscript{39} as shown in Fig. 4.6. Surface transitions $S_1$ and $S_3$ are removed. Peaks associated with oxygen appear at 3.4, 4.9, 7.0, 8.3, 9.5 and 12.8 eV, in complete agreement with the results of Ludeke and Koma.\textsuperscript{40} Previously, on the silicon (111) - (7 x 7) surface, splitting of the surface plasmon peak was observed.\textsuperscript{39} This is due to the appearance of an oxygen-induced transition close to the surface plasmon energy, viz -11 eV.\textsuperscript{39} However, no such splitting was observed on the disordered surface. Instead, the corresponding oxygen transition occurs at a slightly larger transition energy of 12.8 eV.
Fig. 4.6. Loss spectra of the silicon (111) disordered surface with various oxygen coverages.
Previously, several structural models have been proposed for adsorbed oxygen on the silicon (111) surface, in which the formation of silicon-oxygen single or double bond is assumed. In this circumstance, assuming that the final state of the transition (an exciton level) is unchanged, the larger transition energy of this oxygen level indicates that the electrons in the Si-O bond are more tightly bound on the disordered surface. This is likely a result of the more "open" structure on the disordered surface, thereby affording more neighbors for the adsorbed oxygen atom. This explanation is consistent with the observation that on the silicon (100) - (2 x 1) surface, which also has a fairly open structure, the corresponding oxygen transition is at ~13 eV.

This interpretation is further substantiated by the result of oxygen desorption experiments for silicon surfaces (Fig. 4.7). The surface was first saturated with a monolayer of oxygen and then heated to 750°C. The oxygen concentration on the surface was then monitored by AES as a function of time. As can be seen from Fig. 4.7, oxygen is removed faster from the ordered surface than from the disordered surface, which is indicative of the stronger binding of oxygen onto the latter surface. Note that at temperatures less than 700°C, no significant oxygen desorption takes place. No attempt was made to estimate the difference in desorption energies between the two surfaces, because at 750°C, oxygen desorption is accompanied by partial reconstruction on the disordered surface, which would undoubtedly alter the bonding between silicon and oxygen.
Fig. 4.7. The oxygen concentration on silicon surfaces as a function of time after the surfaces have been saturated by a monolayer of oxygen. The substrate temperature is $750 \pm 5^\circ C$. The two curves are scaled to give the same oxygen signal at $t = 0$. 

$\Delta$ Si(III) DISORDERED

$\circ$ Si(III) - (7x7)

$T_{Si} = 750^\circ C$
4.2.3. Conclusion

We have used electron energy loss spectroscopy to study and compare chemisorption processes occurring on both ordered and disordered silicon surfaces of (111) orientation. The studies indicate that the adsorption of acetylene on the silicon (111) - (7 x 7) surface takes place on preferred sites, arising mainly as a result of the overlap between the silicon surface dangling bond and the \( \pi \) orbitals of the acetylene molecules, which are split into two levels as a result of these interactions.

By comparing the difference in the oxygen-related transition at 12.8 eV on the disordered and ordered silicon (111) surfaces, we conclude that the electrons in the silicon-oxygen chemisorption bond are more strongly bound on the disordered surface. This conclusion is substantiated by ELS results on the silicon (100) surface.

The purpose of this study is to examine the effects of an electron donor (acetylene) and an electron acceptor (oxygen) on the electronic surface states of clean silicon surfaces. There are differences, especially in the changes induced by the two different species on the dangling bond transition. It would be of importance to verify the relationship between chemical bonding and electronic surface states. The UPS studies of the bonding of these same adsorbates on the same silicon surfaces would be necessary to provide additional information to establish this correlation.


4.3.1. Specimen Preparation and Special Techniques

The silicon single crystal specimen is the same as that used in the acetylene and oxygen chemisorption experiments. Aluminum was
evaporated onto the silicon surface from a tungsten spiral filament. A stainless steel shutter in front of the evaporator was used to control the aluminum deposition. Auger signals from the deposited aluminum layer and the silicon substrate were monitored during evaporation. The average aluminum coverage was estimated from the attenuation of the silicon Auger peak at 91 eV, assuming an electron mean free path of 6 Å. Backscattering effects are assumed to be small in this estimation of mean coverage.

In taking ELS spectra involving the silicon valence bands, an electron incident energy of ~100 eV was used to obtain maximum surface sensitivity and good signal-to-noise ratio. In order to observe energy losses due to excitations from the silicon 2p core level, its binding energy being 98.9 eV below the Fermi level, the incident electron energy was increased to ~150 eV.

4.3.2. Results

4.3.2.1. Aluminum Deposition at Silicon Substrate Temperatures (T_s) Between 100 and 200°C. In agreement with Lander and Morrison, our LEED observations showed that the (7 x 7) pattern is preserved in the coverage range 0 ≤ θ ≤ 0.5, and that for aluminum coverages greater than 0.5, the one-seventh order spots begin to disappear.

The energy loss spectra of the silicon (111) - (7 x 7) surface with various aluminum coverages are shown in Fig. 4.8. The transitions observed on the clean surface have been identified previously. After depositing 0.75 monolayer of aluminum onto the silicon surface, S3 disappears while S2 only becomes slightly weaker. S1 appears to shift from 1.7 to 1.9 eV. E1 and E2 transition energies increased slightly
Fig. 4.8. Electron energy loss spectra of the silicon (111) - (7 x 7) surface for various aluminum coverages, the latter being deposited at substrate temperatures between 100 and 200°C.
whereas the bulk plasmon energy decreases from 17.2 to 16.9 eV. At \( \theta = 1 \), the bulk plasmon energy shifts further to 16.4 eV and the 1.9 eV transition remains strong.

In order to better understand the above trend of behavior, the corresponding energy loss spectra due to the silicon 2p core level excitation were taken and shown in Fig. 4.9, for \( \theta = 0 \) (the clean silicon (111) - (7 x 7) surface) and \( \theta = 1 \). For the clean (7 x 7) surface, the core-excitation loss spectrum is similar to that of the silicon (100) - (2 x 1) surface. The 99.0 eV peak is due to the empty dangling bond state, 99.8 eV being an exciton level and 100.7 eV being a peak in the silicon-bulk conduction band density of states. At \( \theta = 1 \), the empty dangling bond state disappears and the bulk conduction band peak shifts to 100.5 eV.

Upon further deposition of aluminum up to \( \theta = 2 \) at 100 \( \leq T_s \leq 200^\circ\text{C} \), the energy loss spectrum (Fig. 4.10) shows strong loss peaks corresponding to the aluminum bulk and surface plasmon excitations (15.2 and 10.4 eV respectively). The 1.9 eV transition is also strong at this coverage. Increased deposition of aluminum results in the attenuation of the 1.9 eV peak, the appearance of the 2.5 eV transition and the further growth of the aluminum bulk and surface plasmon loss peak (Fig. 4.11).

As noted before, after the deposition of one monolayer of aluminum (average thickness = 2\( \tilde{A} \)) onto the silicon (7 x 7) surface at a \( T_s \) between 100 and 200\(^\circ\text{C} \), the one-seventh spots are almost non-existent. After annealing at 600\(^\circ\text{C} \) for 30 min, the LEED pattern shows a set of hazy hexagonal reflections around each integral spot (Fig. 4.12).
Fig. 4.9. The electron energy loss spectra due to the silicon 2p core excitation from the clean silicon (111) - (7 x 7) surface (θ = 0 curve) and the same surface with one monolayer aluminum deposited at a substrate temperature of 150°C (θ = 1 curve).
Fig. 4.10. Energy loss spectrum of the silicon (111) - (7 x 7) surface covered by two monolayers of aluminum deposited at a substrate temperature of 100-200°C.
Fig. 4.11. Energy loss spectrum of a 50Å thick aluminum layer deposited onto the silicon (111) - (7 x 7) surface held at 150°C.
Fig. 4.12. LEED pattern obtained after annealing the silicon (111) - (7 x 7) surface with one monolayer of aluminum deposited at $T_s = 100-200^\circ C$. The incident electron energy is 45 eV. Note the hazy hexagonal patch around each integral spot.
The energy loss spectra arising from the silicon valence band and the 2p core are shown in Fig. 4.13(a) and (b). One observes well-developed peaks at 7.0 and 3.2 eV. The bulk and surface plasmon losses occur at 16.7 and 11.2 eV respectively, of 16.4 and 10.3 eV before annealing. Furthermore, the 1.9 eV transition has disappeared. The core-level excitation loss spectrum shows a considerable shift of the conduction band maximum.

4.3.2.2. Aluminum Deposition at $T_s = 600-700^\circ$C. This particular substrate temperature is chosen because aluminum then gives rise to a well-defined surface structure on the silicon surface. The LEED shows a distinct set of hexagonal spots around each integer spot (Fig. 4.14), similar to that obtained by annealing, as discussed in the previous section. The loss spectrum (Fig. 4.15) indicates strong aluminum bulk and surface plasmon losses at 15.1 and 10.3 eV respectively, after deposition of one monolayer of aluminum. The shoulder at 2.5 eV can be attributed to an aluminum bulk transition. Apart from these transitions, the other features of the loss spectrum are similar to those obtained by annealing the silicon (7 x 7) surface with one monolayer of aluminum deposited at $100 < T_s < 200^\circ$C.

4.3.3. Discussion

Aluminum deposition onto the silicon (7 x 7) surface at $100 < T_s < 200^\circ$C removes the $S_3$ transition while $S_2$ weakens slightly. It is difficult to determine from Fig. 4.8 if the 1.9 eV peak is aluminum-induced or a shifted $S_1$ transition. However, the corresponding core-excitation loss spectrum (Fig. 4.9) clearly shows the disappear of the dangling bond state. Therefore the $S_1$ transition is indeed
Fig. 4.13. (a) Energy loss spectra of the silicon (111)-(7x7) surface with one monolayer of aluminum deposited at $T_s = 100-200^\circ$C before (dotted curve) and after annealing at 600$^\circ$C for 30 min (solid curve). (b) The corresponding loss spectrum due to silicon 2p core excitation after annealing.
Fig. 4.14. LEED pattern from the silicon (111) - (7 x 7) surface with one monolayer of aluminum deposited at 600-700 °C. The primary electron energy is 45 eV.
Fig. 4.15. Energy loss spectrum of the silicon (111) - (7 x 7) surface with one monolayer aluminum deposited at 600-700°C.
removed and the 1.9 eV peak can be assigned as an aluminum-induced transition. Moreover, the silicon bulk transitions (E₁ and E₂) shift slightly in energy, indicating that the "bulk" band structure is affected by the presence of aluminum on the surface. However, the influence in bonding is only slight because aluminum can be incorporated substitutionally into the silicon lattice, as shown by the preservation of the (7 x 7) structure and in the coincidence of the silicon E₂ transition with the aluminum transition at 5 eV⁴⁸ (Fig. 4.11). Further, at θ = 1, the bulk plasmon energy is 16.4 eV, which is between that of silicon (17.2 eV) and aluminum (15.3 eV), suggesting an interdiffusion of silicon and aluminum. This behavior was found to prevail in other group III metals, viz Ga and In.⁴⁹-⁵¹ Similar conclusions have been made about the removal of surface states, nature of the 1.9 eV transition and the survival of the silicon bulk transitions, strongly suggesting the similarity in the bonding of aluminum, gallium and indium on the silicon (7 x 7) surface. The UPS studies⁵⁰ indicate that the initial state for the 1.9 eV transition lies approximately 1.5 eV below the valence band maximum and has a strong tail into the midgap region. As is well known in semiconductor electron-hole recombination theory,⁵² any states in the midgap are efficient recombination centres, which are detrimental to many semiconductor devices operations, such as rectifiers, switching, solar cells etc. The existence of these metal-induced gap states has been predicted theoretically.⁵³,⁵⁴

On annealing, the peak at 7.0 eV gradually develops (Fig. 4.3(a)), which explains the apparent incomplete removal of the S₂ transition. The accompanying disappearance of the metal-induced 1.9 eV transition
shows that the nature of the silicon-aluminum interface has changed, as is also evident from the LEED patterns before and after annealing. This observation shows clearly that the interface properties depend on the details of the chemical bonding between the semiconductor and the metal atoms, rather than on the macroscopic notion of work function differences.

The appearance of aluminum bulk and surface plasmons after the deposition of (1) two monolayers of aluminum onto the silicon (7 x 7) surface at 100-200°C or (2) one monolayer of aluminum onto the silicon (7 x 7) surface at 600-700°C is most interesting. Because of the collective nature of plasmon excitations, we would not expect to see these loss peaks from a thin (≥2 monolayers) uniform aluminum layer. Therefore, in both cases, aggregation of aluminum must have occurred. This can be understood as follows: in the initial stage of aluminum deposition in case (1), the aluminum atoms are sitting at certain preferred sites on the silicon (7 x 7) surface, as evidenced by LEED. When all these sites are filled, arriving aluminum atoms will occupy random positions on the silicon surface. Further increase in coverage results in a significant probability of forming clusters with two or more aluminum atoms. There is strong evidence in the study of metal clusters that there exists a critical cluster size (approximately several atoms) above which cluster growth is favorable. Formation of sufficiently large clusters gives rise to the observed plasmon loss peaks. On the other hand, at higher substrate temperatures (≥600°C), the aluminum atoms have high surface mobilities, thereby resulting in a greater chance of forming critical size clusters.
even when the total number of aluminum atoms is smaller than the first case.

It may be noted that annealing a silicon surface with one monolayer of aluminum deposited at 100-200°C does not produce aluminum bulk and surface plasmon loss peaks. The LEED observations indicate that the initial 0.5 monolayer of aluminum atoms are occupying certain preferred sites on the silicon surface. One would expect the aluminum atoms to be more tightly bound in these positions so that they are not mobile enough to participate in the clustering process.

4.3.4. Conclusion

LEED and ELS have been used to study the deposition of aluminum on the silicon (111) - (7 x 7) surface at different substrate temperatures. At substrate temperatures between 100 and 200°C, submonolayer deposition of aluminum results in the removal of silicon electronic surface states and at the same time gives rise to new surface transitions at 1.9, 3.2, 4.9 and 7.0 eV. Shift of the bulk plasmon to lower energies indicates an interdiffusion of silicon and aluminum near the surface. LEED shows that the pattern corresponding to the silicon (111) - (7 x 7) surface structure is preserved up to an aluminum coverage of 0.5 monolayer. Further increase in aluminum coverage results in the disappearance of non-integral spots. When the aluminum deposition takes place at a higher substrate temperature of 600-700°C, a well-defined surface structure is obtained at one monolayer aluminum coverage. Appearance of aluminum bulk and surface plasmon loss peaks in the corresponding ELS spectrum indicate the aggregation of aluminum atoms. The same phenomenon of aggregation also occurs for substrate
temperatures between 100 and 200°C and an average aluminum coverage of two monolayers. This dependence of the interface electronic states on the surface structure dictates a detailed understanding of the chemical bonding between the semiconductor and the metal atoms (microscopic approach) in future studies of metal–semiconductor junctions.

4.4. Suggestions for Further Work

For the three adsorbates studied here, only acetylene does not completely remove the dangling bond surface state on the silicon (111) - (7 x 7) surface. In other adsorption experiments, it has been shown that acetylene is an electron donor. This seems to indicate that the dangling bond surface state of silicon is also an electron donor and hence does not interact very strongly with another electron donor. It would be interesting to pursue this further by studying the interaction of the silicon (111) - (7 x 7) surface with other organic (e.g., benzene and pyridine) and inorganic donor adsorbates (e.g., alkaline metals). Moreover, to confirm the proposal about the split $\pi$ orbitals of acetylene when acetylene is adsorbed onto the silicon (7 x 7) surface, one should look at the photoemission spectrum of the adsorbed acetylene. This should give information on the degree of rehybridization of acetylene on the silicon (111) surface.\(^5\)

The ability of one monolayer of oxygen to remove the dangling bond surface state is of utmost importance in solar cell and other device applications. The dangling bond state is located in the midgap region and is therefore an efficient recombination centre.\(^5\) In a device such as silicon Schottky barrier solar cell, the photogenerated
charge carriers have to come up to the silicon surface and go to the external circuit through a metal contact on the surface. The presence of these surface recombination centres will clearly reduce the cell efficiency. However, by first forming a thin oxide (~10Å) on the silicon surface to remove the recombination centres before putting down the metal contact,\textsuperscript{57-61} the solar cell efficiency can be improved considerably. It is possible, however, that the presence of the thin oxide reduces the reverse saturation current and hence increases the overall cell efficiency. To distinguish between these two possible effects, one can lay down a few monolayers of acetylene on top of the silicon surface before putting down the metal contact and then compare the solar energy conversion efficiencies. The acetylene layer, being an insulator, can reduce the reverse saturation current just like oxygen, but does not remove the recombination centres (dangling bond surface states).

In the case of aluminum deposition on silicon, our ELS data showed the aggregation of aluminum atoms at a mean coverage of one or two monolayers. It would be interesting to follow this process by means of electron microscopy to establish the minimum size of the metal cluster for observing bulk plasmon excitation in electron energy loss spectroscopy. Further, LEED shows that aluminum forms different structures on the silicon (111) - (7 x 7) surface and the measurement of Debye temperatures for these various aluminum structures would give us information on the mean square displacements perpendicular to the silicon surface and hence changes of force constants near the surface for the various structures.
For most metal-silicon Schottky barriers, the barrier height is in the range of 0.6-0.7 eV so that the Fermi level is still about 0.4-0.5 eV above the valence band maximum. However, if a suitable metal-semiconductor combination can be found to give a sufficiently large barrier, the Fermi level will then be close to the valence band maximum. For an n-type semiconductor, this implies that an inversion layer will be formed in which the charge carriers will be holes instead of electrons. With forward bias, a population inversion of electrons can be initiated and hence makes the emission of photons possible in this device.

While most of these studies can be made on other silicon surfaces, the silicon (100) surface deserves special attention on account of its exhibition of the negative electron affinity effect,\(^1\) which can be obtained by putting down half a monolayer of cesium, followed by half a monolayer of oxygen. Apparently a \(\text{Cs}^+ - \text{O}^-\) dipole layer is formed on the surface and causes the electron affinity of silicon to change near the surface region. This is a bona fide surface effect. The surface electronic state changes should be monitored during the formation of this dipole layer. To be useful as a photodetector, one should look at how the photocurrent is affected by ambient gas adsorption and how it can be stabilized. Furthermore, one can replace one or both of the components of the dipole with appropriate electron donors and acceptors to see whether or not such a negative electron affinity effect can be sustained.
REFERENCES


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5. ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION STUDIES OF THE CLEAN (110) and (100) TITANIUM DIOXIDE (RUTILE) CRYSTAL SURFACES.*

5.1. Introduction

Recently, several interesting studies were reported on the photoassisted and photocatalytic reactions of gases on titanium dioxide powder surfaces.1-4 It is established by these studies that light with energy greater than about 3 eV (band gap of TiO₂) plays an important role in such reactions. However, the detailed reaction mechanism is not understood, mostly for two reasons. First, most studies were carried on TiO₂ powders so that essentially all crystal faces were exposed. There is ample evidence from single crystal surface studies5 that chemisorption characteristics change markedly from crystal face of one orientation to another, indicating striking variation of chemical bonding with surface atomic structure. The chemical reaction observed on powders is then a weighted average of reactions taking place on all crystal surfaces, making it difficult to identify the active sites for such photoassisted or photocatalytic reactions. Second, the impurity concentration and the stoichiometry on the TiO₂ surface are usually unknown. To locate the active sites and hence to elucidate the mechanisms for their photoassisted or photocatalytic activities, it is important to characterize and study the chemical reactivity as a function of these parameters.

Another motivation for our titanium oxide studies is that it is one of the few materials that decompose water into hydrogen and oxygen in an electrochemical cell without dissolution, when illuminated by light with energies greater than 3 eV.\textsuperscript{6–9} However, such a photoelectrolysis process can only proceed at an appreciable rate by applying a minimum positive potential of 0.25 eV to the titanium oxide electrode. Without an applied potential, the surface band-bending on the semiconductor electrode is too small to allow an efficient separation of the photo-generated electron-hole pairs,\textsuperscript{8} which appears to be a necessary step in the photoelectrolysis process. An increase in the band-bending of 0.25 eV on the titanium oxide surface without an externally applied potential is desirable in practical applications as solar energy conversion devices. This necessitates a detailed study and understanding of how the surface band-bending can be varied by changing the surface conditions.

The stage is then set for the work to be presented in this chapter. Except for the work of Henrich et al.,\textsuperscript{10} the structure and electronic properties of titanium dioxide single crystal surfaces are relatively unexplored. It is thus important to be able to characterize the surface with as many parameters as possible. In this chapter, we report on studies of clean titanium dioxide (rutile) single crystal surfaces of (110), (100) and (001) orientations. LEED and AES were used to characterize surface structures and compositions respectively. Electron states distributions were studied by ELS and UPS. Information on the work function and surface band-bending was obtained from the photoelectron distribution curves.
5.2. Specimen Preparation

The specimen used was a 99.99% pure undoped titanium dioxide single crystal with the rutile structure. Samples of (001), (110) and (100) orientations, as determined by the Laue back reflection technique, were cut from this crystal and mechanically polished using 1.0 micron Al₂O₃ powders. Gross contaminants on the surface were then removed by etching the specimen in 50°C 5N NaOH solution for 30 min. The specimen was then rinsed in ethanol and mounted on a high density alumina holder, which had a tungsten heater wire located at the back to facilitate the heating of the crystal.

5.3. Selected Properties of Titanium Dioxide (Rutile)

Titanium dioxide can exist in three crystallographic forms, viz anatase, brooklite and rutile. The rutile structure is tetragonal, with \( a = b = 4.59\text{Å} \) and \( c = 2.96\text{Å} \) (Fig. 5.1). Physical properties such as electrical conductivity and dielectric constant are highly anisotropic.

\( \text{TiO}_2 \) is a partially ionic semiconductor. One can consider the valence and conduction bands to be derived mainly from the \( 0(2p) \) and \( \text{Ti}(3d) \) orbitals respectively. The optical band gap is 3.0 eV near room temperature and is indirect. The pure undoped crystal is thus transparent with a yellowish tint.

The phase diagram of the O–Ti system is complicated. Below \(-1830^\circ\text{C} \) (melting point of \( \text{TiO}_2 \)), there exists at least eight intermediate titanium oxides (\( \text{Ti}_n\text{O}_{2n-1}, n = 3 \) to 10) between \( \text{Ti}_2\text{O}_3 \) and \( \text{TiO}_2 \). On reduction by heating in vacuum or hydrogen at 600°C or so for an hour, oxygen is partially lost from the titanium dioxide lattice.
Fig. 5.1. The titanium dioxide (rutile) crystal lattice.
and the crystal becomes blue in color. In this circumstance, transport measurements indicate that the crystal becomes n-type and paramagnetic resonance study shows the presence of Ti$^{3+}$ species.\textsuperscript{11} The oxygen concentration can be restored by heating the reduced crystal in an oxygen atmosphere ($\sim$200 torr) at 600$^\circ$C for 1 hr, as shown by the color change of the crystal from blue to yellow.

5.4. Results

5.4.1. Surface Compositions and Structures

The impurities detected on single crystal surfaces of titanium dioxide after bake-out were sulphur, chlorine, potassium, carbon and calcium. Argon ion bombardment at room temperature removed all these impurities except for a trace of carbon on the surface. Subsequent annealing at 500-600$^\circ$C removed carbon, but resulted in the segregation of potassium and calcium from the bulk to the surface. In order to produce a clean surface, the crystal must be heated to a temperature of 800-900$^\circ$C during argon ion bombardment for $\sim$10\textsuperscript{3} sec before annealing. The Auger electron spectra for clean argon ion bombarded and annealed (at 600$^\circ$C) TiO$_2$ (110) surfaces are shown in Fig. 5.2. The O(510 eV)/Ti(380 eV) Auger peak ratio increases from $\sim$1.3 on the argon ion bombarded surface to $\sim$1.7 on the annealed TiO$_2$ (110) surface. These ratios are fairly reproducible over many sputtering-annealing cycles on different crystal faces of TiO$_2$. In addition, there is a change in the Auger peak shape around 400 eV as a result of argon sputtering.

LEED showed that the (110) surface has a stable (1 x 1) unreconstructed structure after annealing at 600-800$^\circ$C (Fig. 5.3).
Fig. 5.2. Auger electron spectra of (a) argon ion bombarded and (b) annealed TiO$_2$(110) surfaces.
Fig. 5.3. LEED pattern from a clean ordered TiO$_2$ (110) surface at an electron incident energy of 92 eV.
On the other hand, three distinct clean surface structures were found on the (100) surface by annealing the argon sputtered (100) surface at different temperatures (Fig. 5.4). Annealing at 500-600°C resulted in a (1 x 3) surface structure. Further annealing up to 800°C gave rise to a (1 x 5) structure. A surface with a (1 x 7) structure was obtained when the crystal was heated to 1200°C for a few seconds. All three structures are stable at room temperatures, and can be generated by annealing a freshly argon sputtered surface at temperatures indicated above.

AES showed that there is a large variation in the O(510 eV)/Ti(380 eV) Auger peak ratio, decreasing from ~1.7 for the (1 x 3) surface to ~1.5 for the (1 x 5) surface and ~1.3 for the (1 x 7) surface.

The (001) surface restructured to form (110) and (100) facets after annealing the argon sputtered surface, as judged from the LEED patterns at various electron energies (Fig. 5.5). The occurrence of these facets is independent of the annealing temperature over the range 400-800°C. Because of the complexity of the LEED pattern from the faceted surface, it is difficult to tell whether or not the facets are reconstructed.

Prolonged exposure of a clean ordered TiO₂ surface to an electron beam of incident energies 50-200 eV did not induce any observable change in the LEED pattern or the Auger spectrum. However, a 2-min exposure to a 1.6 kV, 20 μA electron beam (typical of AES operation) resulted in observable blurring of the LEED spot pattern.

When a clean well-ordered TiO₂ (110) or (100) - (1 x 3) surface was exposed briefly (30 min to 1 hr) to the ambient atmosphere, the LEED spot pattern was preserved, with some increase in the background
Fig. 5.4. LEED patterns from clean TiO$_2$(100) - (1 x 3), (1 x 5) and (1 x 7) surfaces. The primary electron energies are 110, 62 and 60 eV respectively.
Fig. 5.5. LEED patterns from a clean annealed TiO$_2$(001) surface at various electron energies. Note the changes in the spot pattern on the left side of the picture when the primary electron energy is increased, indicating faceting of the (001) surface.
intensity. The AES indicated only a small carbon contamination (-0.1 monolayer) on the crystal surface. For an argon sputtered TiO₂ surface exposed to the same ambient under similar conditions, the carbon contamination was ≥0.5 monolayer.

5.4.2. Electron Energy Loss Spectroscopy

On the argon ion bombarded TiO₂ (100) surface, the energy loss spectrum (Fig. 5.6(a)) shows five distinct transitions at 13.0, 10.3, 5.6, 3.2 and 1.6 eV. After annealing at 600°C, which results in the formation of the (1 x 3) surface, marked changes show up in the energy loss spectrum, viz the appearance of a loss peak at 8.2 eV, splitting of the 5.6 eV transition, shifting and enhancement of the 3.2 eV and the complete disappearance of the 1.6 eV transition (Fig. 5.6(b)). The (110) surface gives rise to a loss spectrum similar to that of the (100) - (1 x 3) surface. On the (100) - (1 x 5) surface, the energy loss spectrum shows the reappearance of the 1.6 eV transition (Fig. 5.6(c)). The (1 x 7) surface has a loss spectrum similar to that of the (1 x 5) surface, except for a stronger 1.6 eV transition.

From the variation of the amplitudes of the above transitions as a function of primary electron energies, we found that on the (1 x 3) surface, transitions at 8.2, 5.2 and 2.4 eV are all surface sensitive, whereas transitions at 13.5, 10.1 and 5.8 eV are due to bulk TiO₂ interband excitations.¹⁰

High energy electron beams were found to have a significant effect on the energy loss spectra of TiO₂ surfaces. Figure 5.7 shows the energy loss spectra from a freshly annealed (110) surface and the same surface irradiated by a 1600 eV 20μ A electron beam for 100 sec.
Fig. 5.6. Electron energy loss spectra of (a) argon ion bombarded TiO$_2$(100), (b) TiO$_2$(100) - (1 x 3) and (c) TiO$_2$(100) - (1 x 5) surfaces. The spectra were obtained at an electron energy of about 100 eV. Transitions labelled with (*) are surface-sensitive.
Fig. 5.7. Effect of electron beam irradiation on the TiO$_2$(110) surface. The dotted curve is the loss spectrum from a freshly annealed TiO$_2$(110) surface and the solid curve is the spectrum from the same surface after being irradiated by a 1.6 kV, 20 μA electron beam for 100 sec.
The latter spectrum resembles closely to that from an argon ion sputtering surface.

5.4.3. Ultraviolet Photoemission Spectroscopy

The UPS spectra for different titanium oxide surfaces are shown in Fig. 5.8. In agreement with the work of Henrich, et al.,\textsuperscript{10} we found a band gap emission at 0.6 eV below the Fermi level $E_F$ on the argon ion bombarded TiO$_2$ (110) surface (Fig. 5.8(a)). In addition, a peak at $-10.6$ eV (referred to the Fermi level) was found. Annealing at 600°C resulted in the disappearance of these two peaks, together with marked changes in the valence band emission, as shown in Fig. 5.8(b).

The valence band structure of the TiO$_2$(100) - (1 x 3) surface is distinctly different from that of the ordered (110) surface. Note the characteristic cascade structure in the valence band emission at $-5.0$, $-6.4$ and $-7.7$ eV (Fig. 5.8(c)). The UPS spectrum of the (100) - (1 x 5) resembles closely to that of the (1 x 3) surface, except for the increase of the peak at $-5.0$ and $-0.6$ eV relative to the emission at $-6.4$ and $-7.7$ eV (Fig. 5.8(d)). Electron beam irradiation (typical of AES operation) caused smearing of the valence band structure and an increase in the band gap emission around $-0.6$ eV.

It was found that the work function ($= \hbar\nu$ - width of the photoelectron energy distribution) increased from 4.6 eV for the TiO$_2$(110) argon bombarded surface to 5.5 eV for the well annealed (110) and (100) - (1 x 3) surfaces. This result is consistent with that of Henrich, et al.\textsuperscript{10} reported for the (110) surface. From the photoelectron energy distribution, one can further estimate the energy position (referred to the Fermi level) of the bulk valence band maximum...
Fig. 5.8. UPS spectra for various titanium oxide surfaces, obtained with $h = 21.2$ eV at a resolution of 0.35 eV. All energies are referred to the Fermi level: (a) argon ion bombarded (110) surface, (b) ordered (110) surface, (c) (100) - (1 x 3) surface and (d) the (100) - (1 x 5) surface.
by extrapolating the upper valence band to zero emission. Together with the work function measurements and the known values of electron affinity and band gap for TiO$_2$ (4 and 3 eV respectively), we calculated a surface band-bending of $1.7 \pm 0.2$ eV for both the annealed (110) and (100) - (1 x 3) surfaces and $0.9 \pm 0.2$ eV for the argon ion bombardment surface.

5.5. Discussion

The change of oxygen to titanium ratio as a function of surface treatments indicates that oxygen is removed preferentially by argon ion sputtering. On annealing the sputtered surface, oxygen diffuses from the bulk to the surface, thereby increasing the oxygen concentration on the surface. The decrease in the surface oxygen concentration during annealing at temperatures higher than 800°C is due to the removal of oxygen from the surface. Therefore, at any temperature, the surface oxygen concentration is determined by two competing processes, viz the diffusion of oxygen from the bulk to the surface and escape of oxygen from the surface. After using the crystal for many sputtering-annealing cycles, the O(510 eV)/Ti(380 eV) Auger peak ratio on the surface drops to below the normal value of ~1.7 on the (100) - (1 x 3) and (110) surfaces annealed at 600°C. On the (100) surface, this is sometimes accompanied by the occurrence of facets, as a result of excess loss of oxygen from the bulk. When this occurs, the crystal must be reoxidized to establish the original O/Ti ratio.

Oxygen loss from the TiO$_2$ surface as a result of argon sputtering or heating to temperatures 800°C, as observed by AES, is closely
correlated with the appearance of an intense ELS transition at 1.6 eV. The simultaneous change in the titanium Auger peak shape around 400 eV is a strong indication that the oxidation state of titanium has changed as a result of oxygen loss from the surface. Assuming that the atomic ratio of oxygen to titanium is 2 to 1 on the TiO$_2$(100) - (1 x 3) surface, we estimate from the Auger peak intensities the corresponding ratios to be 3 to 2 on the argon sputtered (100) and (100) - (1 x 7) surfaces. This is an indirect evidence of the formation of Ti$^{3+}$ species on the surface as a result of oxygen deficiency, which is reasonable on chemical grounds. Thus, in agreement with the interpretation of Henrich, et al,$^{10}$ this shows that the 1.6 eV transition is due to a Ti$^{3+}$ interband transition. The same 1.6 eV transition was also found on titanium oxide surfaces bombarded by high energy electron beams, implying the loss of oxygen from the surface. Such reducing effects of electron beams have also been observed on vanadium oxide crystal surfaces,$^{16}$ and titanium oxide films.$^{17}$

The appearance of the 1.6 eV ELS transition in the energy loss spectrum of titanium oxide surface bombarded with argon ions or high energy electrons or heated above 800°C correlates very well with the -0.6 eV peak in the corresponding UPS spectrum, which can therefore be assigned to be the initial state for the 1.6 eV ELS transition. The metallic nature of this emission (i.e., non-zero emission up to the Fermi level) is also consistent with the existence of surface Ti$^{3+}$ species because Ti$^{3+}$ has a partially filled d-band and is thus metallic according to the simple band theory.$^{18}$
On the argon ion bombarded surface, a UPS peak at -10.6 eV was found and disappeared on annealing. Because of its large binding energy, this is likely to be the initial state for the 13 eV ELS transition. On annealing, this ELS transition is shifted slightly, but has approximately the same intensity. Thus, the initial state for this transition should still be present. Its absence from the UPS spectra for both the annealed (110) and (100) - (1 x 3) surfaces indicates that this is probably due to the anisotropy of the photoelectron emission from this state. By detecting the photoelectrons emitted in all directions with a spherical collector, Derbenwich\textsuperscript{19} was able to find this peak in the UPS spectrum of the TiO$_2$(110) surface.

The UPS spectra from TiO$_2$ surfaces of different orientations show distinct differences in the density of occupied electronic states, suggesting the existence of surface electronic states or resonances throughout the TiO$_2$ valence bands. However, to date, there are no surface band structure calculations made for the TiO$_2$ crystal (rutile) to allow unambiguous identifications of such surface states and assignments of all the observed electronic transitions.

It is interesting to find that different surface treatments of the TiO$_2$ surface results in drastic changes of the work function and surface band-bending. Argon ion bombardment of a clean ordered (110) surface decreases the work function and band-bending by almost 1 eV. From AES and UPS studies, one finds that the work function and surface band bending of clean TiO$_2$ surfaces decrease monotonically with the surface oxygen concentration. This observation can be explained by the fact that when oxygen is lost from the surface, two electrons
are left in the oxygen vacancy to maintain electrical neutrality. These two electrons are less tightly bound and can easily be excited to the conduction band. Oxygen vacancies become in effect donor centres. This increases the surface free electron concentration, thereby causing a decrease in the surface band-bending. Clearly, these changes have profound effects on the interaction between the semiconductor surface and adsorbates, as demonstrated by the different contamination rates of clean ordered TiO$_2$(110) surface and the same surface bombarded with argon ions, on exposure to the ambient atmosphere.

In photo-induced reactions where the transport of photogenerated charge carriers at the surface (e.g., transport of holes to the TiO$_2$ surface during photoelectrolysis) is the rate-determining step, it is desirable to increase the surface band-bending to allow a rapid charge transport to and away from the semiconductor surface. The ability to change the work function and surface band-bending by different surface treatments such as argon ion bombardment and annealing, as demonstrated here, may be of importance in controlling photo-induced surface reactions.

5.6. Conclusion

In this study we demonstrated the ability of LEED and various electron spectroscopy techniques to study and characterize single crystal surfaces of titanium dioxide (rutile). LEED showed that both the (110) and (100) surfaces are stable, with the latter surface giving rise to three distinct surface structures, viz (1 x 3), (1 x 5) and (1 x 7), that appear by annealing an ion-sputtered (100) surface
at temperatures ~600, 800 and 1200°C respectively. The (001) surface is unstable and restructures to give (110) and (100) facets.

Argon ion bombardment was found to remove oxygen preferentially from the TiO₂ surface. Subsequent annealing treatments indicate that at a given annealing temperature, the surface oxygen concentration is determined by the relative rates of oxygen diffusion from the bulk to the surface and the escape of oxygen from the surface. Indeed, the formation of the (100) - (1 x 3), (1 x 5) and (1 x 7) surface structures correlates with the decrease in the O(510 eV)/Ti(380 eV) Auger peak ratio from ~1.7 to ~1.3 as shown by AES.

The (110) and (100) - (1 x 3) surfaces give similar energy loss spectra, with surface-sensitive transitions at 8.2, 5.2 and 2.4 eV. An additional ELS transition at 1.6 eV was found in the (100) - (1 x 5) and (1 x 7) surfaces. On the argon ion bombarded surface, a well defined ELS transition at 1.6 eV was found, arising from Ti³⁺ interband transitions. The UPS spectra from these surfaces indicate that the band gap emission at ~0.6 eV can be attributed to be the initial state for the 1.6 eV ELS transition on argon ion bombarded TiO₂ surfaces.

Low energy (50-200 eV) electron irradiation does not have any observable effects on the surface composition, structure and electron state distribution of clean TiO₂ surfaces. However, initially clean and well ordered TiO₂ surfaces are disordered by electron beams normally used in Auger analysis, as demonstrated by LEED, energy loss and UPS. The work function and band-bending of clean ordered TiO₂(110) and (100) - (1 x 3) surfaces were found to be 5.5 and 1.7 eV respectively. They decrease with oxygen loss from the surface, as a result of argon
ion bombardment or annealing at temperatures greater than 800°C, to 4.6 and 0.9 eV respectively. This change is likely to have effects on photoassisted or photocatalytic surface reactions. In the light of these findings, it would be of importance to be able to vary the work function and surface band-bending of the semiconductor surface by different surface treatments and study the chemical reactivity as a function of these parameters. Such information is basic to the understanding of the activities of these surfaces in photoassisted or photocatalytic reactions.
REFERENCE

15. Surface band-bending = E_{C,s} - E_{C,b} = (E_{C,s} - E_F) + (E_F - E_{C,b})
   where E_{C,s} and E_{C,b} are the energy positions of surface and bulk
   conduction band minimum respectively. The first term is equal
   to (work function-electron affinity) and the second term is equal
   to (E_F - E_{V,b} - the energy of the band gap), where E_{V,b} is the
   bulk valence band maximum. In this calculation, we do not include
   the possibility of electron affinity changes because the electron
   affinity for both Ti metal and TiO_2 is 4 eV and we do not expect
significant deviations for titanium oxides of intermediate compositions.


6. CHEMISORPTION OF WATER ON TITANIUM OXIDE SURFACES: ROLE OF SURFACE Ti$^{3+}$ SPECIES

6.1. Introduction

In the previous chapter, we have made a complete characterization study of titanium oxide surfaces of different orientations, which shows the possible existence of Ti$^{3+}$ species on titanium oxide surfaces when they are argon ion bombarded or heated above 800°C. Moreover, it has been demonstrated in a rather crude manner that the argon disordered surface is more reactive than one that has been annealed. Such difference in the reactivity of these two surfaces were also confirmed by some recent electron stimulated desorption studies. The natural question would be: can this difference in reactivity be attributed to the surface disorder or the presence of surface Ti$^{3+}$ species? While there is no difficulty of knowing whether or not the surface is ordered (at least in the realm of the electron coherence length, which is ~100Å), the problem of determining the presence of Ti$^{3+}$ species is not entirely transparent. In Chapter 5 we rely on the comparison of relative Auger intensities to argue the existence of Ti$^{3+}$ species on the argon ion bombarded surface, and by correlating the changes of the Auger spectrum with the 1.6 eV ELS transition, we tentatively establish that the 1.6 eV transition arises from Ti$^{3+}$. However, it is possible that other titanium species of lower oxidation states, such as Ti$^{2+}$ and Ti$^{+}$, can contribute to this ELS transition. Therefore, before we can establish the cause of reactivity on titanium oxide surfaces, we have to prove (or disprove) that Ti$^{3+}$ is the only species which can give rise to the observed 1.6 eV transition. This was achieved by studying the oxidation of titanium metal and monitoring
the intensity of the 1.6 eV transition as a function of the Ti oxidation state. These studies verify that the 1.6 eV transition is a legitimate fingerprint for Ti^{3+}. By using this fingerprinting technique, it was further demonstrated that Ti^{3+} species can be generated by depositing monolayer amounts of titanium metal onto an oxygen rich titanium dioxide surface, e.g., the TiO_2(100) - (1 x 3) surface.

Having established this crucial point of identifying surface Ti^{3+} species, we then used UPS to study the chemisorption of water on three different types of clean titanium oxide (100) surfaces:

1. the (100) - (1 x 3) surface, which has no detectable concentration of Ti^{3+},

2. the (100) - (1 x 7) surface, which has surface Ti^{3+} present,

and

3. the argon ion disordered (100) surface which has surface Ti^{3+} present,

Results of these studies suggest that Ti^{3+} species are responsible for the activity of titanium oxide surfaces and that the chemical nature and bonding of the adsorbed water layer to the substrate clearly depend on the concentration of Ti^{3+} on the surface.

6.2. Specimen Preparation and Special Techniques

The titanium metal specimen was prepared by spark-cutting a one mm slice from a 99.99% pure titanium single crystal rod. The titanium single crystal sample was oriented in the [0001] direction by the Laue Technique and mechanically polished using 1.0 micron Al_2O_3 powders. It was then etched in dilute nitric acid and rinsed in ethanol before being introduced into the vacuum chamber. The titanium crystal was
held in place by two spot-welded titanium foil contacts through which current was passed to facilitate direct heating of the titanium crystal.

A titanium dioxide single crystal of (100) orientation was prepared in the same way as described in Chapter 5. But in this study, it was not mounted on an alumina holder, but was held on a piece of tantalum foil. The titanium dioxide specimen could be heated to 600°C by passing a current of 30 amps through the tantalum foil which heated the crystal indirectly. The reasons for this arrangement will be made clear below.

Titanium metal deposition was made in a similar manner to aluminum, which was described in Chapter 4. The evaporation rate was approximately 2.5Å (one monolayer) of titanium metal per minute. The average thickness was determined from the attenuation of the oxygen Auger signal at 510 ev, assuming an electron mean free path of 10Å.

In water adsorption studies, the titanium oxide specimen was held at room temperature and water was admitted into the chamber through a 2 mm i.d. dosing probe in front of the titanium oxide specimen to provide a high local pressure. To ensure the removal of dissolved gases in water, the water sample was subjected through at least one pump-freeze-thaw cycle before being introduced into the chamber.

Thermal desorption studies were carried out after adsorption of water onto the titanium oxide specimen, in which the specimen was heated indirectly by the tantalum heater foils. Typically a current of 20 amps was passed through the tantalum foil. The temperature rise was not linear and was typically 2.5°C/sec at 150°C and 1°C/sec at 250°C. In order to increase the sensitivity of the thermal desorption
experiments, the specimen was rotated in front of the quadrupole mass spectrometer during heating and the poppet valve separating the chamber and the pump was closed down to get an effective pumping speed of a few litres per second for water. Since the tantalum foil was heated up very quickly, all the water that was adsorbed on the foil was desorbed in about 10 to 20 sec and this water desorption signal did not interfere with that from the titanium oxide surface, which acquired a maximum water desorption signal at least 50 sec after the tantalum foil was heated. On the other hand, if the titanium oxide crystal was placed in an alumina holder, as described in Chapter 5, the alumina holder would also adsorb water and in subsequent thermal desorption, the holder would also be heated up, but relatively slowly compared with the tantalum foil in the present case, and thus give a water desorption signal which may interfere with that from the titanium oxide crystal.

6.3. Results and Discussions

6.3.1. Identification of Ti$^{3+}$ Species: Oxidation of Titanium Metal

Gross impurities on the surface were first removed by argon ion bombardment. Then the crystal was annealed at 300°C in an oxygen flow-through mode, with local oxygen pressure \( \sim 10^{-5} \) torr, to remove residual carbon on the surface and sulphur segregating from the bulk to the surface. The oxide that formed on the surface could subsequently be flashed off at 600°C to produce a clean ordered (1 x 1) surface.

The oxidation was performed at a substrate temperature of 300°C and an oxygen pressure of \( 10^{-6} \) to \( 10^{-7} \) torr. The O(510 eV)/Ti(380 eV) Auger peak ratio reached a constant value of 1.1 at an oxygen exposure of \( 10^3 \) L or greater. We expect the top layers of the titanium metal
to be oxidized all the way to titanium dioxide, as has been found in some photoemission work. The fact that the $O/Ti$ Auger peak ratio (1.1) is less than that on the TiO$_2$(100) - (1 x 3) surface (~1.7) indicates that not all the titanium atoms within the electron mean free path (~10Å) are oxidized. Assuming that the oxide growth is in the [001] direction, we estimate an oxide thickness of roughly 6Å, which then acts as a diffusion barrier against further oxidation. This is supported by the constancy of the $O$(510 eV)/Ti(180 eV) Auger peak ratio with further oxygen exposure up to $10^5$ L.

In Fig. 6.1 we show the intensity of the 1.6 eV ELS transition as a function of the $O/Ti$ atom ratio, the latter being obtained directly from the $O$(510 eV)/Ti(380 eV) Auger peak ratio, assuming that an $O$(510 eV)/Ti(380 eV) Auger peak ratio of 1.1 corresponds to an $O/Ti$ atomic ratio of two. The 1.6 eV ELS transition acquires a sharp maximum at an $O/Ti$ atom ratio of ~1.5 and drops rapidly to zero on either side of the maximum. The $O/Ti$ atom ratio of 1.5 corresponds to the composition of Ti$_2$O$_3$. This unique feature of the 1.6 eV transition thus justifies its use as a fingerprint for the existence of surface Ti$^{3+}$ species.

6.3.2. Deposition of Titanium on the TiO$_2$(100) - (1 x 3) Surface

In the above experiment, we generated Ti$_2$O$_3$ from the oxygen-deficient side of the O-Ti system, viz Ti. It is also possible to produce Ti$^{3+}$ species from the oxygen-rich side, viz from the TiO$_2$(100) - (1 x 3) surface, by reduction. This has been done previously by argon ion bombardment or high temperature annealing, which preferentially removes oxygen. The alternative way is to reduce the TiO$_2$(100) - (1 x 3)
Fig. 6.1. The intensity of the 1.6 eV ELS transition as a function of the O/Ti atom ratio.
surface by titanium deposition. Figure 6.2 shows a comparison of the Auger, energy loss and uv photoemission spectra of the TiO$_2$(100) - (1 x 3) surface before and after the deposition of one monolayer of titanium, deposition being made with the TiO$_2$(100) - (1 x 3) surface held at room temperature. AES shows the expected decrease of the O/Ti ratio, and the gradual emergence of the doublet around 410 eV. The energy loss spectrum shows again the appearance of the 1.6 eV transition, the initial state of which is clearly seen as a peak at 0.6 eV below the Fermi level in the corresponding UPS spectrum. All these spectra are almost identical to those obtained from argon ion bombarding the (100) - (1 x 3) surface and point to the existence of Ti$^{3+}$ species as a result of titanium deposition.

6.3.3. UPS Studies of the Chemisorption of Water

Figure 6.3 shows the UPS spectra of the TiO$_2$(100) - (1 x 3) surface before and after the exposure to $10^5$ L of water at room temperature. Three new peaks emerge at -6.1, -7.8 and -11.2 eV relative to the Fermi level. Also there is an accompanying work function decrease of 0.8 eV, indicating that the upward band-bending has decreased. Assuming a constant electron affinity of 4.2 eV, the band bending drops from 1.7 eV to 0.9 eV ($\pm 0.2$ eV) on adsorption of water. This observation is certainly not inconsistent with the results from electrochemical cell experiments, in which the flat-band potential for TiO$_2$ near pH = 7 is $\sim$0.6 eV without any light illumination. The difference can be due to the low water coverage on the titanium dioxide surface ($\sim$0.5 monolayer) in our experiments.
Fig. 6.2. A comparison of the Auger, electron loss and photoemission spectra of the TiO₂(100) - (1 x 3) surface before and after the deposition of one monolayer of titanium at room temperature. The spectra after Ti deposition resemble closely to those of the argon ion bombarded (100) surface.
Fig. 6.3. The UPS spectra of the TiO$_2$(100) - (1 x 3) surface before and after a water exposure of 10$^5$ L at room temperature.
After heating the TiO$_2$(100) - (1 x 3) surface at 800°C for approximately 2 hr, a (1 x 7) surface structure is developed and the O(510 eV)/Ti(380 eV) Auger peak ratio drops from 1.7 on the (1 x 3) surface to 1.4-1.5. After 10$^5$ L water exposure, the (1 x 7) surface gives rise to four new emission peaks in the UPS spectrum (Fig. 6.4). There is a work function decrease of 0.4 eV, corresponding to a band bending change from 1.5 eV to 1.1 eV on adsorption of water. Further, the UPS emission at -0.6 eV due to Ti$^{3+}$ is reduced as a result of water adsorption, suggesting the partial removal of surface Ti$^{3+}$ species.

The removal of Ti$^{3+}$ on the surface is demonstrated more clearly on the argon ion bombarded TiO$_2$(100) surface (Fig. 6.5). Three water-induced emissions are found at -4.2, -7.5 and -10.1 eV, which are quite different in energy positions from those produced by water adsorption on the (1 x 3) surface. For the same water exposure of 10$^5$ L, the magnitude of the increase in emission is about a factor two larger than that for the (1 x 3) and (1 x 7) surfaces, indicating that the sticking probability of water on the argon ion bombarded surface is larger than that for the other two surfaces. The work function changes is small (-0.1 eV) and the upward band-bending changes from 0.5 eV to 0.4 eV.

On all three surfaces, the adsorption of water causes the work function to decrease. However, one notices that the work function change induced by chemisorption of water varies considerably on these surfaces, the change being smaller on surfaces which have higher surface Ti$^{3+}$ concentrations, e.g., the argon sputtered TiO$_2$(100) surface. This cannot be accounted for as being due to the lower coverage of
Fig. 6.4. The UPS spectra of the TiO$_2$(100) - (1 x 7) surface before and after a water exposure of $10^5$ L at room temperature.
Fig. 6.5. The UPS spectra of the argon sputtered TiO$_2$(100) surface before and after a water exposure of $10^5$ L at room temperature.

Ar sputtered TiO$_2$(100) + $10^5$ L H$_2$O

$\phi = 4.4$ eV

$T = 300^\circ$K

$\Delta \phi = -0.1$ eV

Electron Binding Energy, eV

N(E)

Ar sputtered TiO$_2$(100)

$\phi = 4.5$ eV

-10.1

-7.5

-4.2

$E_F = 0$
water on the argon sputtered surface because photoemission indicates that exactly the reverse is true. As discussed above, adsorption of water removes Ti$^{3+}$ as seen from the depopulation of the Ti$^{3+}$ d-band emission at -0.6 eV in the UPS spectrum. Therefore, Ti$^{3+}$ is re-oxidized back to Ti$^{4+}$. It is interesting to note that in aqueous solution, oxidation of Ti$^{3+}$ to Ti$^{4+}$ also occurs. This abstraction of an electron from Ti$^{3+}$ by the adsorbed water implies that the chemical nature of the adsorbate will be different from molecular water, and hence will result in different work function changes.

In order to look at the changes in the chemical nature of the adsorbed water on different titanium oxide surfaces, we obtain (from Figs. 6.3 through 6.5) photoemission difference curve for each titanium oxide surface by subtracting the clean surface spectrum from the one with an adsorbed layer of water. This is shown in Fig. 6.6. The difference curve of adsorbed water on the TiO$_2$(100) - (1 x 3) surface compares very closely with the gas phase molecular water photoemission spectrum$^8$ (the dotted curve in the top panel of Fig. 6.6). By aligning the -11.2 eV emission in the difference curve with the lb$_2$ molecular orbital of water, we obtain a relaxation shift of 2.2 eV. The lb$_1$ orbital (topmost lying orbital) suffers an additional shift of 0.6 eV towards larger binding energy, probably as a result of chemical bonding to the substrate. But the overall similarity of this difference curve with the UPS spectrum of gas phase water is a strong evidence that the water is adsorbed associatively on the (1 x 3) surface.

Things change drastically on the (1 x 7) surface, which is still ordered, but has a detectable concentration of surface Ti$^{3+}$. The
Fig. 6.6. Photoemission difference curves of water adsorbed on three different titanium oxide surfaces. These curves are obtained directly from Figs. 6.3, 6.4 and 6.5 and are re-scaled.
difference curve (middle panel of Fig. 6.6) for the adsorbed water has four peaks, rather than three in molecular water. The three lower lying peaks are shifted slightly (0.1-0.4 eV) with respect to the corresponding peaks on the (1 x 3) surface. A new peak develops at -4.8 eV. This suggests that part of the adsorbed water is either decomposed or bound to the surface differently. With further depletion of oxygen from the titanium oxide surface, as in the case of an argon sputtered surface (bottom panel of Fig. 6.6), the water-induced peaks shift to smaller binding energies and finally a three-peak spectrum is developed. One is tempted to associate this spectrum with water bound to the surface in a different manner from the (1 x 3) surface. Indeed, when we align the $1b_2$ orbital of water with the -10.1 eV emission peak in the difference spectrum, we find chemical bonding shift of 1 eV and 0.2 eV for the $3a_1$ and $1b_1$ orbitals respectively. The different bonding of water to the substrate, as exemplified by the chemical shift of the $3a_1$ orbital, may account for the different work function changes. However, the only discomforting thing about this explanation is that in order to line up the -10.1 eV peak with the $1b_2$ orbital, which is assumed not to participate in the bonding with the substrate, we require an enormous relaxation shift of 3.8 eV. To the best of our knowledge, relaxation shift of this magnitude has never been observed. The other possibility is that the adsorbate is not water, but a different chemical species. We will pursue this point further in a later section. But in any case, the close correlation of the development of the water-induced spectra with the surface Ti$^{3+}$ concentration is sufficient evidence for the dominant chemical
activity of Ti$^{3+}$ on titanium oxide surfaces.

While the experimental conditions in all our studies are quite remote from those in titanium dioxide electrochemical cell experiments, it is worthwhile to note that the semiconductor specimens are reduced to give sufficient conductivity in both cases. The photoelectrode surface, as a result of this reduction treatment, will also have some Ti$^{3+}$ present. The degradation of activity of photoelectrodes as a function of time is found to be related to the photoelectrode preparation and reduction procedure. From these observations, it appears that the photoelectrolysis process occurring in wet solutions is related somehow to the concentration of surface Ti$^{3+}$. We will return to this crucial point in Chapter 7.

For a TiO$_2$(100) - (1 x 3) surface in contact with vacuum, the surface band-bending is >1.5 eV (Section 5.4) so that one would expect very efficient separation of electron-hole pairs once they are generated, e.g., by illuminating with band gap radiation. However, when the titanium oxide surface is in contact with water, water acts as an electron donor, as demonstrated clearly in this work, causing the band-bending to decrease. This explains why a minimum positive bias of 0.25 volt must be applied to the titanium oxide electrode to give sufficient band-bending on the surface for sustained photolysis of water in the electrochemical cell. In principle, it is possible to increase the band-bending by adsorption of electronegative species such as oxygen$^{10}$ or anions$^{11}$ onto the surface. But no work was done to correlate the photoelectrolysis efficiency with the adsorption of these species onto the semiconductor electrode, either because
of undesirable side reactions which inhibit the evolution of hydrogen,\textsuperscript{12} or the instability of the adsorbate under photoelectrolysis conditions.\textsuperscript{11}

6.3.4. Flash or Thermal Desorption Studies of Adsorbed Water on Titanium Oxide Surfaces

While UPS studies have identified that surface Ti\textsuperscript{3+} species are active and interact with water, the nature of the chemisorbed water is not entirely certain. To pursue this point further, we have performed thermal desorption studies of water adsorbed on titanium oxide surfaces of varying stoichiometry, the adsorption being made at room temperature and with the same exposure of 10\textsuperscript{5} L. The oxygen to titanium ratio was varied by argon sputtering and annealing either in vacuum or in an oxygen atmosphere, typically of 10\textsuperscript{-6} torr.

Figure 6.7 shows a series of such thermal desorption profiles of water (m/e = 18). On the oxygen-rich titanium oxide surface (topmost curve in Fig. 6.7), there are two distinct peaks at \(-150^\circ\text{C}\) and \(-230^\circ\text{C}\). As the O/Ti ratio is decreased, which means a simultaneous increase in the surface Ti\textsuperscript{3+} concentration, as evidenced by ELS and UPS, the 230\textsuperscript{0}C-peak shifts slightly to higher temperatures and dominates over the 150\textsuperscript{0}C-peak. At an O(510 eV)/Ti(380 eV) Auger peak ratio of 1.30 (the lowest value we have ever reached), the thermal desorption profile shows a dominant peak at 250\textsuperscript{0}C and a weak shoulder at \(-150^\circ\text{C}\). Note also the greater amount of water desorption on the oxygen-deficient surface, which is another indication of the greater sticking probability of water on Ti\textsuperscript{3+}-rich surfaces.

In our previous discussion of the UPS results of water adsorbed on titanium oxide surfaces, we concluded that on the Ti\textsuperscript{3+}-rich surface,
Fig. 6.7. Thermal desorption profiles of water adsorbed on titanium oxide surfaces of different stoichiometries. The heating rate is 2.5°C/sec at 150°C and 1°C/sec at 150°C.
water is either bonded to the surface differently (e.g., through a different molecular orbital), or decomposed to some other species, which have similar UPS spectra as water. The thermal desorption results, as shown in Fig. 6.7, are certainly in agreement with this observation. To distinguish between these two possibilities, we have resorted to compare with results obtained by other techniques. Results of electron stimulated desorption measurements\(^1\) suggests that water is either dissociated when adsorbed on the argon sputtered titanium oxide surface into hydroxyl groups and hydrogen, or is in a metastable state which easily dissociates. We have also performed some thermal desorption experiments of hydrogen for water adsorbed on titanium oxide surfaces and have indeed detected the desorption of hydrogen in an amount which is ten times larger than that expected from the cracking of water in the mass spectrometer ionizer. Other thermal desorption and infrared adsorption studies\(^13-17\) on titanium oxide powders show that the lower temperature desorption peak (at 150°C) in the desorption profile of water arises from chemisorbed molecular water. As the temperature is raised above 200°C, the intensity of the infrared adsorption peak around 1600 cm\(^{-1}\), corresponding to OH stretching, remains. Above 300°C, the H-O-H bending disappears and the O-H stretching begins to decrease in intensity. This shows clearly that the higher temperature peak (at 250°C) observed in thermal desorption is due to water resulting from the condensation of hydroxyl groups.

Combining all the results from UPS, thermal desorption, electron beam stimulated desorption and infrared absorption studies, we have strong evidence that water is decomposed on a Ti\(^{3+}\)-rich titanium oxide
surface into hydroxyl groups and hydrogen, while Ti$^{3+}$ is oxidized to Ti$^{4+}$.

6.4. Conclusion

The major findings presented in this chapter can be summarized as follows: (1) The 1.6 eV ELS transition arises solely from Ti$^{3+}$ interband transition. Its correlation with the -0.6 eV UPS emission shows that this UPS emission can also be used as a fingerprint for Ti$^{3+}$. (2) Titanium deposition on the TiO$_2$(100) - (1 x 3) surface generates Ti$^{3+}$, as detected by the appearance of the 1.6 eV ELS transition. Schematically, one can write:

$$\text{Ti} + 3 \text{TiO}_2 \rightarrow 2 \text{Ti}_2\text{O}_3$$

or

$$\text{Ti}^0 + 3 \text{Ti}^{4+} + 4 \text{Ti}^{3+}$$

(6.1)

(3) The TiO$_2$(100) - (1 x 3) surface, which has no Ti$^{3+}$ present, is relatively inert and water is adsorbed associatively on this surface. However, on a Ti$^{3+}$-rich titanium oxide surface, which can be obtained by argon ion bombardment or heating above 800°C, the chemisorbed water is decomposed to hydroxyl groups and hydrogen, while Ti$^{3+}$ is oxidized to Ti$^{4+}$. Again, this is schematically represented by:

$$\text{H}_2\text{O} + \text{Ti}^{3+} \rightarrow \text{H}_2\text{O}^{(ads)} + \text{Ti}^{4+}$$

or

$$\text{H}_2\text{O}^{(ads)} \rightarrow \text{OH}^{(ads)} + \text{H}^{ads}$$

(6.2)

(4) Adsorption of water on all titanium oxide surfaces causes the band bending to decrease which accounts for the requirement of a positive
bias to the titanium oxide electrode to photoelectrolyze water at an appreciable rate in the electrochemical cell.
REFERENCES


4. The effective pumping speed for water, S, at any setting of the poppet valve can be determined as follows. A constant leak of water into the chamber is established and the pressure rise, Δp, is determined as a function of time, t. One can show that

\[ \Delta p = \Delta p_{\text{max}} (1 - e^{-St/V}) \]

where \( \Delta p_{\text{max}} \) is the maximum pressure rise for a constant leak and V is the volume of the chamber. Let

\[ t = t_{1/2} \quad \text{when} \quad \Delta p = 1/2 \Delta p_{\text{max}}. \]

Then

\[ S = \frac{V}{t_{1/2}} \ln 2. \]


7. PHOTOLYSIS OF WATER ON SEMICONDUCTING METAL OXIDE SURFACES

7.1. Introduction

Ever since the first report of the photoelectrolysis process, many semiconductors (WO₃, Fe₂O₃, Si and SnO₂, to name a few) have been tried as photoanodes,¹⁻⁴ most of which require an extra positive bias to acquire sufficient band-bending for initiating and sustaining the photodecomposition of water in the electrochemical cell at any appreciable rate. If one uses these semiconductors for photolysis of water on a "half-cell" basis, it is not at all certain how these external potentials could be applied. Electro-negative species or anions can be adsorbed to increase the band-bending, but have not been explored at this moment. At zero bias, TiO₂ can give oxygen evolution when illuminated with bandgap radiation, provided that the platinum counter-electrode has a sufficiently large area.⁵ Strontium titanate and potassium tantalate, on the other hand, decompose water into hydrogen and oxygen at relatively fast rates compared with TiO₂ at zero external potential.⁶,⁷a

One would, therefore, expect strontium titanate and potassium tantalate, as well as titanium dioxide to a certain extent, to be good candidates for the "half-cell" photodecomposition of water. Indeed, it was demonstrated recently that platinized N-type strontium titanate and potassium tantalate evolve oxygen and hydrogen from alkaline aqueous solution when irradiated with band gap radiation. The irradiated portions of the metal oxide behave as the photoanode and the dark platinized portions behave as the cathode.⁷b
However, the occurrence of photolysis of water in a "half-cell" under a nominal water pressure of one atmosphere does not necessarily mean that the same reaction should be observable under ultra-high vacuum conditions. If the reaction rate is proportional to the partial pressure of water, then even when one works with an absurdly high water partial pressure of $10^{-4}$ torr in the UHV chamber, then the reaction rate will still be down by seven orders of magnitude. Therefore, in order to observe any effects at all under low pressure conditions, the most efficient semiconductors should be used, viz titanium dioxide and strontium titanate. Because of the similarity between the electronic band structure of titanium dioxide and that of strontium titanate\textsuperscript{8,9} especially in the occurrence of the $-0.6$ eV UPS emission on reduction,\textsuperscript{8} which signifies the presence of Ti$^{3+}$, we believe that the mechanism of the photodecomposition of water on titanium dioxide and strontium titanate, if it occurs at all under low pressure conditions, should be similar. Therefore, we have used titanium oxide single crystals of (100) orientation as a simple model system to study the effects of light on the electronic structure of the semiconductor and the adsorbate. This choice is also dictated by our better knowledge of the properties of the water/titanium oxide system.

In our attempts to look for water photodecomposition reactions on titanium oxide and strontium titanate surfaces, an estimate has been made for the typical signals one may expect to get. In the electrochemical cell under the best possible conditions, approximately 1 c.c. of oxygen is evolved from the strontium titanate electrode (1 cm\textsuperscript{2}) per hour in the presence of UV photon flux of $\sim 10^{17}$ cm\textsuperscript{-2} sec\textsuperscript{-1}. 
This is equivalent to $7.5 \times 10^{15}$ molecules/cm$^2$-sec. Let us assume that the reaction proceeds at a rate proportional to the partial pressure of water and that we are detecting this oxygen evolution by means of a mass spectrometer. Suppose we work at a water pressure of $10^{-5}$ torr. This would give an oxygen evolution rate of $10^8$ molecules per second per cm$^2$ of the semiconductor surface. This is equal to $3.2 \times 10^{-12}$ litre-torr per second. With the pump throttled down to give an effective pumping speed of 1 litre per second for oxygen, this translates to a pressure rise of $3.2 \times 10^{-12}$ torr. The typical noise level in our mass spectrometer detection system corresponds to a pressure fluctuation of approximately $1 \times 10^{-12}$ torr. This is very close to the noise margin. Therefore, in our photolysis studies, to obtain the maximum signal, all possible measures such as specimen preparation, mass spectrometer positioning, light focusing etc must be taken.

The format of this chapter is as follows. In Section 7.2, the sample preparation and experimental techniques used are described. Effects of ultra-violet light illumination on titanium oxide surfaces and the adsorbed water layer are described in Sections 7.3.1, 7.3.2 and 7.3.3. Photodecomposition studies of water on single crystals of titanium oxide and strontium titanate are presented and discussed in Section 7.3.4. Based on these experimental observations, a photolysis mechanism is proposed and outlined in Section 7.4. A summary of the findings, possible implications of the present work and suggestions for further research are included in Section 7.5.
7.2. Sample Preparation and Experimental Techniques

A titanium dioxide single crystal sample of (100) orientation was mounted on a tantalum holder in the same way as described previously in Chapter 6. To ensure that one is generating a titanium oxide surface which is free of Ti$^{3+}$ after annealing at 600°C, an energy loss spectrum was taken with an electron beam of energy in the range of 20-40 eV. Absence of the 1.6 eV ELS transition under normal sensitivity settings was considered as a proof for the absence of Ti$^{3+}$ on the surface. On the other hand, Ti$^{3+}$-rich titanium oxide surfaces were generated by argon-ion sputtering. In order to obtain an approximately constant and reproducible concentration of surface Ti$^{3+}$ species, the conditions for argon-ion sputtering were standardized, viz 2 keV, 10 μA argon ion beam for a period of 10$^3$ sec.

Adsorption of water on titanium oxide crystal surfaces was carried out in a similar manner as outlined in Chapter 6. The UPS spectra were taken on clean surfaces (Ti$^{3+}$-absent and Ti$^{3+}$-rich surfaces) and the same surfaces with absorbed water before and after $10^{-4}$ sec of ultra-violet light illumination.

The strontium titanate single crystal, orientation (001), was first reduced at 800°C for half an hour in a hydrogen furnace and then mechanically polished through successive grits to a 1.0 micron finish. It was then etched in 50°C 5N NaOH solution for 30 min and rinsed with ethanol before being mounted on a tantalum holder. The active surface area was approximately 0.25 cm$^2$.

Band gap radiation was provided by a 500-watt high pressure mercury lamp, which was water- and air-cooled during maximum power
operation. The ultra-violet light was transmitted to the specimen through a sapphire window (upper cut-off energy being about 6 eV). To make the best possible use of the emitted uv light, a 20-cm focal length quartz lens was used to focus the light onto the sample surface so that only the sample and part of the holder were illuminated. An infrared filter, made from filling a quartz cell with nickel sulphate solution, was placed between the mercury uv source and the quartz focusing lens to absorb the heat and transmit the uv. This arrangement thus limits the temperature rise of the specimen due to radiation heating to less than +30°C and hence avoids any spurious effects due to thermal desorption from either the sample, the holder or the walls of the vacuum chamber. The total photon flux was approximately $2 \times 10^{16}$ cm$^{-2}$ before focusing and $\sim 10^{17}$ cm$^{-2}$ after focusing, as measured by a calibrated Eppley pyrheliometer. The approximate wavelength response was checked by inserting various filters and measuring the corresponding photo-induced mass spectrometer signal.

The quadrupole mass spectrometer was re-positioned in such a way that during illumination, the sample normal was approximately 30° from both the light beam and the axis of the quadrupole mass spectrometer, which was about 12 cm away from the sample. This increases the detection sensitivity substantially. In this circumstance, part of the photo-induced signal detected by the mass spectrometer was due to gas molecules going directly from the sample surface to the mass spectrometer ionizer and part of it due to scattering of the desorbed species into the ionizer. The first part is more or less independent of the pumping speed of the system, while the second part
can be increased by throttling the poppet valve to give very low pumping speeds (~ few litres per second), thereby giving more chance for the desorbed species to be scattered into the mass spectrometer ionizer before being pumped away. A schematic diagram showing the relative positions of the mercury light source, the quadrupole mass spectrometer and the sample is indicated in Fig. 7.1.

7.3. Results and Discussions

7.3.1. Effects of Light on the TiO\textsubscript{2}(100) - (1 x 3) Surface

The TiO\textsubscript{2}(100) - (1 x 3) surface was prepared by argon ion sputtering and subsequent annealing at 600°C, as described previously in Chapter 5. The LEED observations showed well defined integral and non-integral diffraction spots. To make sure that the electron beam used in LEED observations did not induce any significant reduction of the titanium oxide surface\cite{10,11}, the crystal was annealed again at 600°C for 1 to 2 min. An energy loss spectrum was then taken using a 20-40 eV electron beam to ensure that the 1.6 eV Ti\textsuperscript{3+}-induced energy loss transition did not appear. Usually, this procedure is sufficient to generate a well-ordered TiO\textsubscript{2}(100) - (1 x 3) surface with no Ti\textsuperscript{3+} present.

After the surface was illuminated with a focused beam of uv light for periods ranging from 20 min to 1 hr, no changes could be observed in the uv photoemission and Auger electron spectra. However, after a 25-min exposure of the (1 x 3) surface to the uv light from the mercury lamp, a small shoulder at 1.6 eV could be clearly seen in the ELS spectrum, using a 20 eV electron beam (Fig. 7.2). The possible reducing effect of the 20 eV electron beam can be ruled out because
Fig. 7.1. Experimental arrangement for studying photodecomposition of water on semiconducting metal oxide surfaces. LEED optics, CMA etc. are not shown in this figure, but are arranged as shown in Fig. 3.1.
Fig. 7.2. The energy loss spectrum of the TiO$_2$(100) - (1 x 3) surface (a) before and (b) after 15 min of uv light illumination. Light intensity is $\sim$10$^{16}$ - 10$^{17}$ cm$^{-2}$sec$^{-1}$. Electron energy used in here is $\sim$20 eV.
in order for the 1.6 eV ELS transition to grow to the level shown in Fig. 7.2 without uv light, it requires at least 20 min continuous electron beam exposure at 20 eV while the total time required to take the two spectra shown in Fig. 7.2 is less than 30 sec. In the absence of both uv light and continuous electron beam exposure, no 1.6 eV ELS transition could be observed after waiting 30 min.

Therefore, by associating the 1.6 eV ELS transition with the appearance of surface Ti$^{3+}$ species, we firmly establish that uv light illumination of the TiO$_2$(100) - (1 x 3) surface generates Ti$^{3+}$, according to the following reactions:

\[ \text{hv} + \text{e}^- + \text{h}^+ \quad \text{(generation of electron-hole pairs)} \quad (7.1) \]

\[ \text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+} \quad \text{(reduction of Ti}^{4+} \text{ to Ti}^{3+}) \quad (7.2) \]

The reverse reaction, viz the oxidation of Ti$^{3+}$ back to Ti$^{4+}$, is going on simultaneously during light illumination:

\[ \text{Ti}^{3+} + \text{h}^+ \rightarrow \text{Ti}^{4+} \quad (7.3) \]

Since the light is absorbed uniformly over a rather large region (~1000$\AA$ thick) and Ti$^{4+}$ ions are the majority species, one would expect the rate of generation of Ti$^{3+}$ according to Eq. (7.2) to be almost constant in time. On the other hand, the rate of oxidation of Ti$^{3+}$ back to Ti$^{4+}$ is simply proportional to the concentration of Ti$^{3+}$. From these arguments, one can set up the following rate equation:

\[ \frac{d}{dt}[\text{Ti}^{3+}] = A - B[\text{Ti}^{3+}] \quad (7.4) \]
where $A$ and $B$ are rate constants, depending on light intensities, for Eqs. (7.2) and (7.3) respectively. Solving, we have

$$[\text{Ti}^{3+}] = \frac{A}{B} (1 - e^{-Bt}) \quad (7.5)$$

Figure 7.3 shows the intensity of the 1.6 eV ELS transition as a function of illumination time, with the intensity normalized to one at time $t = 60$ min. The experimental data points can be well fitted by Eq. (7.5), assuming $B = 1.2 \times 10^{-3}$ sec$^{-1}$. The surface may have a slightly lower concentration of Ti$^{3+}$ than the bulk because the electric field in the surface space charge region tends to draw more holes to the surface and favors the oxidation of Ti$^{3+}$ to Ti$^{4+}$ over the reverse reaction.

When the light is turned off, one would expect the conversion of Ti$^{3+}$ back to Ti$^{4+}$ by electron injection to the conduction band, and therefore a decrease in the Ti$^{3+}$ concentration. This should occur in the bulk because of the proximity of the highest lying electronic level of Ti$^{3+}$ ($\approx E_F$) to the conduction band minimum. However, on the surface, the Fermi level (or the Ti$^{3+}$ level) is approximately 1.3 eV below the conduction band minimum.$^{12a}$ This makes the probability of electron injection into the conduction band very small so that on the surface, the Ti$^{3+}$ concentration is practically constant after the light is turned off, as shown in Fig. 7.3. The energetics of this process is shown schematically in Fig. 7.4. Note that although Ti$^{3+}$ can be converted to Ti$^{4+}$ by hole capture from the valence band, there are not many holes available at room temperature in the n-type titanium oxide crystal studies here.
Fig. 7.3. Intensity of the 1.6 eV ELS transition as a function of time $t$. The intensity is scaled such that it is equal to one at $t = 60$ min. Note the increase in intensity as the uv light is turned on and its constancy after the uv light is turned off at $t = 60$ min. The curve is plotted from Eq. (7.5), assuming $B = 1.2 \times 10^{-3}$ sec$^{-1}$. 
Fig. 7.4. Energetics of the Ti$^{4+}$ - Ti$^{3+}$ conversion on the TiO$_2$(100) - (1 x 3) surface. In order for Ti$^{4+}$ to be converted to Ti$^{3+}$, an electron is required. This comes from the electron-hole pair generation by light illumination, hence the requirement of band gap energy (3 eV). In order to oxidize Ti$^{3+}$ to Ti$^{4+}$, an electron has to go from the Ti$^{3+}$ level ($\approx E_p$) to the conduction band minimum. This requires approximately 1.3 eV.
It is interesting to make a qualitative estimate of the amount of surface Ti\textsuperscript{3+} generated when the steady state is reached. The intensity of the 1.6 eV ELS transition at steady state is approximately one to two hundred times smaller than that for the surface that has been argon sputtered for $10^3$ sec at an argon beam energy of 2 keV and current $10^{-6}$ A. This implies that we have $10^{12} - 10^{13}$ Ti\textsuperscript{3+} per \text{cm}^2 on the titanium oxide surface at steady state, assuming that there are $10^{14} - 10^{15}$ Ti\textsuperscript{3+} per \text{cm}^2 on the argon sputtered surface. This has an interesting consequence. Suppose we start with a titanium oxide crystal which has been reduced in such a way that there are greater than $10^{13}$ Ti\textsuperscript{3+} species per \text{cm}^2 on the surface. On illumination, the Ti\textsuperscript{3+} concentration should be decreased until it reaches the steady state value of $10^{12} - 10^{13}$ \text{cm}^{-2}. Ideally, this prediction can simply be tested by measuring the intensity of the 1.6 eV ELS transition as a function of light illumination time on such a specimen. However, in practice, it is difficult to look for 1-2\% change in energy loss measurements.

Let us assume that for some reason, the rate of the photoelectrolysis process occurring on the titanium oxide photoelectrode is, besides other factors, proportional to the surface concentration of Ti\textsuperscript{3+} species. The above argument would imply that if one starts with a heavily reduced titanium oxide electrode, light illumination would cause a decrease in the surface Ti\textsuperscript{3+} concentration and hence a proportional drop in the photocurrent or gas evolution rate. On the other hand, if one starts with a lightly reduced specimen, the reaction rate would slowly increase with illumination time until a steady state is reached.
This completely explains the degradation of reactivity for titanium oxide electrodes as a function of time. This is an important guideline in our attempt to understand the mechanism of photolysis of water on semiconductor surfaces.

7.3.2. Effects of Light on Water Adsorbed on the TiO$_2$(100) - (1 x 3) Surface

The TiO$_2$(100) - (1 x 3) surface was first prepared and the photoemission spectrum was taken. The surface was then exposed to 3000 L of water at a water partial pressure of $5 \times 10^{-6}$ torr. The difference spectrum between the clean surface and the same surface with adsorbed water is shown in Fig. 7.5(a), and is characteristic of molecular water, as discussed in Chapter 6. The surface was subsequently exposed to uv illumination for approximately $10^4$ sec. The difference spectrum, referenced to the clean (1 x 3) surface, was obtained and shown in Fig. 7.5(b).

It is clear from Fig. 7.5 that the difference spectra, due to the extra photoelectron emission induced by the water adsorbed, are similar before and after $10^4$ sec of uv illumination, which corresponds to about $10^{21}$ photons cm$^{-2}$. Thermal desorption showed that the total amount of water adsorbed on the (1 x 3) surface was approximately $3 \times 10^{13}$ molecules cm$^{-2}$. The UPS measurements should be sensitive to 10% change in the surface concentration of adsorbed water molecules, assuming that the water-induced emission is proportional to the surface coverage of water. Absence of any observable change in UPS indicates that any photon-induced change in the chemical state of water must be occurring with a cross-section less than $10^{-22}$ cm$^2$. Of course we
Fig. 7.5. Effect of light on the difference spectrum of water adsorbed on the TiO$_2$(100) - (1 x 3) surface.
here assume that any change in the chemical state of water will result in an appreciably different photoemission spectrum.

Because of the low absorption coefficient of water for light in the energy range between 3 and 4 eV, it is expected that the direct interaction between water and the photons would be extremely small. The strongest interaction probably occurs indirectly through the photo-generation of electron-hole pairs and subsequent interaction of the hole with water adsorbed on the semiconductor surface. Since the quantum efficiency (defined as the number of electrons or holes flowing per second/the number of photons incident upon the semiconductor surface per second) is on the order of $10^{-2}$ to $10^{-4}$, depending on the photon energy used, the number of holes arriving at the titanium oxide surface is $10^{13} - 10^{15}$ cm$^{-2}$sec$^{-1}$. This puts an upper limit on the interaction cross-section for the photogenerated hole and the molecularly adsorbed water to be $10^{-18} - 10^{-20}$ cm$^2$.

7.3.3. Effects of Light on Water Adsorbed on the Ti$^{3+}$-Rich Titanium Oxide Surface

The Ti$^{3+}$-rich titanium oxide surface was prepared by argon ion bombardment of the TiO$_2$(100) - (1 x 3) surface with a 2 keV, 10 lA argon ion beam for a period of $10^3$ sec. The presence of Ti$^{3+}$ species was checked by UPS, which showed the Fermi edge emission at -0.6 eV. The difference spectrum between the argon sputtered surface and the same surface after a 3000 L water exposure is shown in Fig. 7.6(a). The surface was then subjected to $10^4$ sec of uv light illumination, after which the difference spectrum, referenced again to the argon sputtered surface, was obtained and shown in Fig. 7.6(b).
Fig. 7.6. Effect of light on the difference spectrum of water adsorbed on the Ar-sputtered TiO$_2$(100) surface.
The photoemission difference spectrum shown in Fig. 7.6(a) is very close to what we obtained previously and the three peaks are explained as due to emissions from OH⁻ and H. After $10^4$ sec of light illumination, there is an overall increase in the secondary electron background and there appears to be an increase in the intensity of the -7.3 eV peak. There is also a simultaneous work function increase of 0.4 eV. In a separate experiment, it was found that $10^4$-sec uv light illumination of a clean Ti³⁺-rich titanium oxide surface (i.e., without adsorbed water) results in a work function increase of 0.3 eV and an increased UPS emission at -7.0 eV. Therefore, the change in the water-induced photo-emission difference curve as a result of light illumination is probably due to residual gas adsorption. On the ordered (1 x 3) surface, this does not happen because of the relative inertness of the surface to residual gas adsorption.

At this point, we cannot exclude the possibility of a slow photo-induced reaction on the semiconductor surface, but simply remark that under the present experimental conditions and reaction rates, any gaseous products coming from the photo-induced reaction will be very small in quantity. For example, let us assume that in the $10^4$-sec period, a total of $10^{12}$ molecules of water are decomposed to give hydrogen and oxygen. This gives an average rate of $10^8$ molecules of hydrogen/sec, this gives a pressure rise of $3.2 \times 10^{-13}$ torr. This is not an easily detectable quantity.

7.3.4. Photodecomposition of Water on Titanium Oxide and Strontium Titanate Surfaces

We first attempted to observe photodecomposition of water on single crystal surfaces of titanium oxide and strontium titanate,
both of which have been partially reduced and were argon sputtered before water adsorption. This was done because in Section 7.3.2, we demonstrated that light has no observable effect on water adsorbed on ordered and Ti$^{3+}$-absent titanium oxide surface. Argon sputtering increases the surface concentration of Ti$^{3+}$ which in turn dissociates the adsorbed water into OH$^-$ and H. Hopefully, these species would interact directly with band gap radiation or via the photogenerated charge carriers.

Two methods of water exposure were tried. One is to give the semiconductor surface a fixed water exposure of 10$^5$ L with the pump valve closed and then pump away the water at the end of the exposure. The other method is to fill up the vacuum chamber with water vapor up to 1-2 x 10$^{-5}$ torr, with the pump throttled down to a very low pumping speed (~2 litres/sec). In both cases, the surface was illuminated with uv light and the partial pressures of H$_2$ (m/e = 2), H$_2$O (m/e = 18) and O$_2$ (m/e = 32) were monitored. No change (i.e., any possible change would be less than 1.0 x 10$^{-12}$ A, which is approximately equal to 5 x 10$^{-13}$ torr) in the partial pressure of any of these species was observed.

In a recent report, it was demonstrated that the inability to see gas evolution under our experimental conditions is probably due to insufficient surface area. By using strontium titanate powders to increase the effective surface area, hydrogen and oxygen evolution were observed when the SrTiO$_3$ powders were illuminated by light with energy greater than the band gap. Although water was photodesorbed at the same time, the amounts of hydrogen and oxygen detected are
at least two orders of magnitude greater than could be accounted for by the fragmentation of water in the mass spectrometer. It was further discovered that UV illumination of the powder surface with a co-adsorbed layer of H₂O and D₂O results in the evolution of HD and D₂, which indicates the scission of OH bonds of the adsorbed water. This is consistent with our observation made on Ti³⁺-rich titanium oxide surfaces and verifies our proposal on the decomposition of water into hydroxyl groups and hydrogen (Eq. 6.2). Also, it was found that reduced SrTiO₃ always gives hydrogen and oxygen at higher rates when illuminated. This again is consistent with the higher activity of Ti³⁺ species.

From the pressure rise, it was estimated that the rate of evolution of hydrogen to be typically 10⁹ molecules/cm²·sec. This is approximately seven orders of magnitude lower than that obtained from electrochemical cell experiments. This difference can arise from two sources: (1) poor electrical contacts due to high specimen resistivity may reduce rate of charge transport and hence reaction rates; (2) the overall reaction probability may be pressure-dependent (see Section 7.4).

Based on this experiment result on strontium titanate, one would expect titanium oxide and potassium tantalate to be also able to decompose water in this "half-cell" configuration, provided sufficiently large active areas of the semiconductors are used. For titanium oxide, because of its small band-bending compared with SrTiO₃ under the same conditions (about 0.2 eV or less), the rate of hole transport to the surface and hence the reaction rate are lower by a factor of \(\exp\left(-\frac{0.2 \text{ eV}}{kT}\right)\). At room temperature, this translates into a rate decrease of approximately three orders of magnitude. Therefore, with the same
light intensity and surface area, titanium oxide is expected to give a pressure rise of $10^{-13}$ amps for hydrogen under low pressure conditions. Potassium tantalate, on the other hand, should give an easily detectable signal under the same conditions because it has larger band-bending at the surface.

7.4. Mechanism of the Photodecomposition of Water

In this section, we formulate and propose the mechanism of the photodecomposition of water on titanium oxide and strontium titanate surfaces. This proposal is based on all the available experimental information on titanium oxide and strontium titanate, both in dark and in the presence of light. The mechanism proposed is assumed to be similar for both titanium oxide and strontium titanate, for reasons discussed in Section 7.1.

7.4.1. The Mechanism

Let us assume that we start with either one of the semiconducting metal oxide, i.e., titanium oxide or strontium titanate (hereafter referred to as SMO), which has some Ti$^{3+}$ on the surface. On adsorbing water to the SMO surface, part of the water is decomposed by the surface Ti$^{3+}$ species into hydroxyl groups and hydrogen, i.e.,

$$\text{Ti}^{3+} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^{\ddagger}_{\text{ads}} + \text{Ti}^{4+} \quad (7.6)$$

$$\text{H}_2\text{O}^{\ddagger}_{\text{ads}} \rightarrow \text{OH}^{\ddagger}_{\text{ads}} + \text{H}^{\ddagger}_{\text{ads}} \quad (7.7)$$

Some of the evidence for this reaction has been described in Chapter 6. Additional evidence is available from the photo-desorption of water and the evolution of HD$^{15}$ from the SMO surface when illuminated with uv (Section 7.3.4).
At the same time, the undecomposed water has to maintain a certain equilibrium with OH\(^-\) and H\(^+\), i.e.,

\[
\text{H}_2\text{O}_{(\text{ads})} = \text{OH}^- + \text{H}^+
\]  \hspace{1cm} (7.8)

When equilibrium is established in the dark, there are finite amounts of OH\(^-\) and H on the surface, which accounts for the results of thermal desorption experiments (Section 6.3.4). The concentration of surface H\(^+\) is expected to be too small for any significant contribution to thermal desorption. To increase surface H\(^+\) concentration, one needs to force the reaction to the right in Eq. (7.8). This can be achieved by removing the OH\(_{(\text{ads})}\) by neutralization. At room temperature without light, this would require the injection of an electron into the conduction band. The minimum energy required is equal to the Schottky barrier height at the SMO surface, i.e., the energy difference between the Fermi level and the conduction band minimum at the surface. At one monolayer water coverage, this is approximately 0.2 eV on the argon-sputtered titanium oxide surface and probably larger for strontium titanate. Therefore, this electron injection process proceeds slowly at room temperature.

However, when this water/SMO system is illuminated by band gap radiation, electron hole pairs are generated uniformly in the near surface region

\[
h\nu \rightarrow e^- + h^+
\]  \hspace{1cm} (7.9)

Because of the surface space charge potential, holes are swept to the surface and neutralize the OH\(_{(\text{ads})}\) species
This neutralization process is equivalent to electron-hole recombination and takes place most efficiently at localized states with energy near the mid-gap region. For argon sputtered or heavily reduced titanium oxide surface, there is a band of occupied states due to Ti\(^{3+}\) extending from the valence band maximum to the Fermi level (see Chapter 5) and probably provides the recombination centres for these OH\(^{−}\)(ads) species. Therefore, surface Ti\(^{3+}\) species control both the water decomposition (Eqs. (7.6) and (7.7)) and also the OH\(^{−}\)(ads) neutralization (Eq. (7.10)).

The OH radicals then recombine to form hydrogen peroxide which then decomposes into water and oxygen

\[
2\text{OH(ads)} \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2
\]  

The non-stoichiometric ratio of hydrogen to oxygen measured in our experiment is evident from Eq. (7.11), as a result of the intermediate formation of hydrogen peroxide. Also part of the water may be desorbed from the surface due to hydrogen peroxide decomposition.

From Eq. (7.6), Ti\(^{3+}\) is removed from the surface by the adsorbed water. This is replenished by the Ti\(^{4+}\) capturing the photogenerated electron, as shown in Section 7.3.1.

\[
\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}
\]  

As the photogenerated electron drifts to the metal contact, H\(^+\) is neutralized and hydrogen is released from the surface.

\[
\text{H}^{+}(\text{ads}) + \text{e}^- \rightarrow \text{H(ads)}
\]
If there is no metal contact, the surface potential barrier may be too high for the electron to go to the surface, which is necessary for neutralizing the $H_{\text{ads}}^+$ species. Wrighton, et al.\textsuperscript{7b} has demonstrated that in the electrochemical cell, the use of a single strontium titanate electrode without any metal contact or counter-electrode will not give any observable water photodecomposition. In our experiment, a slow hydrogen evolution, as described by Eq. (7.14) may still be possible, due to the presence of some $H_{\text{ads}}$ species present on the surface from Eq. (7.7).

Some of the adsorbed water is present as $H_2O^-$ (Eq. (7.6)) which will be neutralized and subsequently be desorbed during illumination

$$H_2O^- + h^+ \rightarrow H_2O$$  \hspace{1cm} (7.15)

This is another contribution to the water photodesorption signal.

### 7.4.2. Extension to Other Semiconductors

The above mechanism relies on the presence of surface $\text{Ti}^{3+}$ as recombination centres for the efficient neutralization of $\text{OH}^-$ species, and the ability of light to regenerate these $\text{Ti}^{3+}$. For $\text{Fe}_2\text{O}_3$ and $\text{KTaO}_3$, $\text{Fe}^{2+}$ and $\text{Ta}^{4+}$ would be present when oxygen is lost from the lattice. These lower oxidation state metal ion species would play similar roles as $\text{Ti}^{3+}$ in $\text{TiO}_2$, viz decomposition of water and neutralization of $\text{OH}^-$ species. Therefore, in a search for other semiconductors for photodecomposition of water, one of the basic requirements would be the presence of stable surface electronic levels close to the midgap region as neutralization centres.
7.5. Conclusion and Suggestions for Further Research

In this chapter, we have shown conclusively that strontium titanate can be used to decompose water in the gas phase without using any liquid electrolyte and external potential. The roles of surface Ti$^{3+}$ and light are clearly demonstrated. Surface Ti$^{3+}$ species decompose water into hydroxyl groups and hydrogen and act as centres for OH$^{-}$ neutralization. Water clearly removes these surface Ti$^{3+}$ species. To sustain the photodecomposition of water, light is needed to replenish these Ti$^{3+}$ species and at the same time provides electrons and holes for neutralization of OH$^{-}$ and H$^{+}$ species. Based on the observation reported in Chapters 5 through 7, a mechanism is proposed to explain the photodecomposition of water on semiconducting metal oxide surfaces when illuminated by band gap radiation.

The success of the cited experiment has tremendous implications. The ability to observe these photo-induced reactions under UHV conditions implies that one can use conventional surface analytical techniques for surface characterization and study the reactivity as a function of these characterization parameters such as surface structure, composition and electronic state distribution. This would help us to elucidate the mechanisms involved, as has been demonstrated here. Moreover, one is then not limited by conventional electrochemical cells using aqueous electrolytes to work at 100°C or less. The potential of performing chemical reactions in the gas phase at higher temperatures to increase reaction rates and avoid diffusion limitations of reactants and products is certainly a great advantage over electrochemical cell systems.
Therefore, the immediate experiment that one should try is to increase the temperature of the SMO specimen above 100°C and study the evolution rate of hydrogen and oxygen when illuminated by band gap radiation as a function of temperature. This experiment should be feasible because hydroxyl groups are not expected to desorb completely from the surface at less than 250°C. One would expect a higher reaction rate and hydrogen and oxygen yields to be closer to the stoichiometric ratio of 2 to 1 due to the more complete decomposition of hydrogen peroxide at elevated temperatures.

Since the photodecomposition process involves the transport of photogenerated electrons and holes to and away from the SMO surface, it is possible that one can increase the reaction rate by increasing the conductivity or carrier mobility of the specimen. It would be interesting to see the effect of improving the electrical contact between the SMO and the metal.

While one may be able to improve the gas evolution rate by working at substantially higher water partial pressure, the usefulness of strontium titanate is limited in that it has a large band gap of 3.2-3.3 eV at room temperatures. There are less than 10% of the solar spectrum with photon energies greater than 3.2 eV. To be useful in solar energy conversion, one has to look for other smaller band-gap semiconductors. Recently, it was shown that by adsorbing appropriate dye molecules on titanium dioxide surfaces, it is possible to produce photocurrents with light of energy less than the normal bandgap of TiO₂.¹⁶ It is important to investigate how this adsorbed dye layer
affects the electronic properties of the substrate (semiconductor + water). Both the occupied and empty electronic levels for the combined semiconductor/water/dye system should be mapped out by both UPS and ELS to determine whether or not the surface can be photo-sensitized, i.e., the dye can bring the effective band gap to the visible region of the solar spectrum.

There are two basic problems untackled in our studies. First, we have been making close analogy between reactions occurring on titanium dioxide and strontium titanate surfaces, based on their similar electronic structures. It would be necessary to supplement this analogy by similar characterization studies on strontium titanate single crystal surfaces. Second, the Ti$^{3+}$ - Ti$^{4+}$ conversion has been monitored by UPS and ELS in our studies. However, the ideal technique would be to use XPS to determine the energy positions of the core levels (e.g., Ti - 2p) of titanium. In this way, one can observe the oxidation state changes as a result of argon sputtering, annealing and water adsorption.

Obviously, one is not limited to the study of photodecomposition of water alone. The presence of hydroxyl groups (OH$^-$) due to water decomposition and subsequent neutralization by photogenerated holes to the hydroxyl radical (OH) provide an interesting reaction substrate. The hydroxyl radical OH is very reactive and is thus capable of performing many thermodynamically uphill reactions, e.g., reduction of nitrogen to ammonia at low pressures, carbon monoxide or dioxide to hydrocarbons etc. This opens up a new field of catalysis studies using hydroxyl radicals on SMO surfaces as substrates.
The recently developed technique of high resolution electron energy loss spectroscopy can be used to study the decomposition of water when adsorbed on oxygen-rich and Ti$^{3+}$-rich titanium oxide or strontium titanate surfaces. It would be especially interesting to see how the spectra will develop as a result of light illumination. Further, molecular beam scattering of water vapor from oxygen-rich and Ti$^{3+}$-rich SMO surfaces, with or without band gap radiation, can be used to study the rate and energetics of the Ti$^{3+}$-water reactions. Finally, the product distributions should be monitored as a function of sample temperature, concentration of surface Ti$^{3+}$ etc so that one can control and optimize such distributions.
REFERENCES

12. (a) The surface band-bending is approximately 1.5 eV. The Fermi level lies 0.2 eV above the bulk conduction band minimum. Therefore, the Fermi level is approximately 1.3 eV below the surface conduction band minimum.
   (b) The cross section A is defined by the equation \( \frac{dn}{dt} = An\phi \), where \( n \) is the number of water molecules on the surface and \( \phi \) is the photon flux.
ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my research advisor Professor Gabor A. Somorjai for his guidance, encouragement and numerous insights in doing successful and high quality research throughout my graduate career. I want to thank Dr. Wigbert J. Siekhaus for first introducing me to this exciting field of surface science and his many illuminating discussions on academic and philosophical matters. I am most grateful to Wei-Jen Lo for his close co-operation throughout the work on semiconducting metal oxides, to Drs. Larry L. Kesmodel and Peter C. Stair for introducing me to the work of acetylene and ethylene chemisorption on platinum surfaces. I also wish to thank all the technical staff in MMRD; especially Emery Kozak, Weyland Wong, Jim Severns, Del Peterson, Phil Eggers and Glenn Baum, for their assistance at various stages of the research. I would also like to thank every friend and colleague in our research group from whom I learn many exciting aspects of surface and catalysis science and of course, Millie Schonborn, without whose typing expertise many of the publications would not have been possible, and Jean Wolslegel for unscrambling my thesis manuscript into a beautiful masterpiece. This work was done with support from the U. S. Energy Research and Development Administration.
APPENDIX: ULTRAVIOLET PHOTOEMISSION STUDIES OF ACETYLENE AND ETHYLENE ADSORPTIONS ON THE PLATINUM (111) SURFACE: CORRELATIONS WITH LEED STUDIES

The chemisorption of acetylene on the platinum (111) single crystal surface has been studied using low energy electron diffraction (LEED) by several authors.\textsuperscript{1-3} It has been found that under conditions of low acetylene exposure (approximately 3 langmuirs), the adsorbed acetylene forms a well-ordered overlayer structure with a diffraction pattern characteristic of a (2 x 2) unit mesh. By measuring the diffraction beam intensities from this system as a function of electron energy,\textsuperscript{3} it was found that the adsorption takes place in two steps: acetylene was first adsorbed at 300°K into a metastable state, followed by a conversion into another more stable state upon heating to 350°K. Both structures show the characteristic (2 x 2) diffraction patterns which can be distinguished only through changes in the diffraction beam intensity profiles. By adsorbing ethylene on the same platinum (111) crystal surface, followed by low energy (~100 eV) electron beam exposure, the initially disordered adsorbate yields the same (2 x 2) diffraction pattern with the intensity vs electron energy curves identical to those of the more stable acetylene structure.\textsuperscript{3} Whether the disordered adsorbate is ethylene or acetylene prior to ordering with the aid of the electron beam could not be ascertained by LEED studies.

Recent dynamical LEED calculations by Kesmodel, et al.\textsuperscript{4,5} have shown that in the metastable structure, acetylene appears to sit approximately on the top of the platinum surface atom at 2.45 Å above the surface\textsuperscript{4} and that in the more stable structure, acetylene
sits at a triangular site 1.95 Å above the plane of the platinum (111) surface, the carbon atoms coordinating at covalent bonding distances to three surface platinum atoms. Therefore, in the transformation from the metastable to the stable structure, acetylene simply "rolls" down from the atop site to the three-fold triangular site.

In the past few years, ultraviolet photoelectron spectroscopy (UPS) has been quite successfully used to study the chemisorption state of adsorbed molecules on transitional metal surfaces. It is of importance to apply UPS to investigate the chemical bonding of adsorbate systems that have also been studied by LEED. In this way, the structure and bonding of the surface species can be established more completely and with greater certainty. For this reason, we have undertaken the investigation of the UPS spectra of chemisorbed acetylene on the platinum (111) surface employing experimental conditions that are identical to those utilized in LEED studies. Further, by comparing the room temperature chemisorbed ethylene photoemission spectrum with that of the more stable acetylene structure, we can identify the chemical state of the adsorbed ethylene molecule on the platinum (111) surface.

All the experiments were performed in an ultrahigh vacuum chamber as described in chapter 3. The platinum (111) single crystal surface was cleaned by argon ion sputtering and heating to 1000°K in an oxygen pressure of 1 x 10⁻⁷ torr. Surface characterization was performed by LEED, Auger electron spectroscopy and UPS. The energy of the photoemitted electron was analyzed with a double-pass CMA operated at a constant energy resolution of 0.15 eV. The angle of incidence of
the photons on the sample was 75° from the axis of the CMA. Two orientations of the sample have been used with sample normal direction either 75 or 67.5° from the incident photon beam. The results obtained were independent of these two orientations. In order to remove the acetone invariably present in small concentrations in research grade cylinders of acetylene, a molecular sieve trap held at dry-ice temperature (195°K) was introduced between the gas cylinder and the gas-manifold of the system.

In Fig. 1(a) we show the photoemission difference spectrum N(E) for platinum (111) after exposure to 3 L acetylene for hν = 21.2 eV with a sample temperature of 300°K. The binding energy was measured from the Fermi energy Ef. We observed two acetylene-derived emissions at -3.8 eV and -8.2 eV of approximately equal intensities. The accompanying work function change measured by the changes of the low energy cut-offs of the photoelectron spectra was -0.4 eV. In agreement with the results of Stair and Somorjai,3 a distinct (2 x 2) diffraction pattern could be seen by LEED. After heating this chemisorbed acetylene to 350°K for 1 hr and cooling it down to room temperature, we found a different more stable chemisorbed acetylene state characterized by a new photoemission difference spectrum that is shown as N(E) in Fig. 1(b). A new emission peak appeared at -5.5 eV and the relative intensities and positions of the peaks characteristic of the metastable surface structure have changed. The higher binding energy peak shifted from -8.2 eV to -7.8 eV while the lower binding energy peak shifted from -3.8 eV to -4.0 eV. The ratio of these two emission intensities was about 3 to 1. The LEED pattern showed the same (2 x 2) ordered
Fig. 1. Photoemission difference curves $\Delta N(E)$ relative to $E_F$ for (a) metastable acetylene state after 3L acetylene exposure on the Pt(III) surface at room temperature (300°K). Preliminary identification with the molecular orbitals of gas phase acetylene is indicated; (b) the stable acetylene state after heating the acetylene adsorbed Pt(III) surface to 350°K for an hour. Work function change $\Delta \phi$ in (a) and (b) is -0.4 eV.
overlayer structure except that the spot intensities changed, consistent with the findings of the previous LEED analysis. After saturating the platinum (111) surface with $10^3$ L acetylene exposure, the UPS spectra remained unchanged. However, the long range $(2 \times 2)$ ordering was destroyed, and the work function change was higher (≈1.0 eV) for this saturated condition.

Figure 2 shows the difference spectra for chemisorbed ethylene at 300°K with 3 L exposure on the platinum (111) surface. The adsorbate was disordered and gave a very similar photoemission to that of Fig. 1(b). When exposed to a 100 eV electron beam for 100 sec, we observed by LEED a $(2 \times 2)$ pattern gradually developing across the whole surface. The photoemission spectrum for this $(2 \times 2)$ structure was identical to that in Fig. 2 or Fig. 1(b). The accompanying work function change was −0.5 eV. All the experiments have been repeated using two different platinum (111) single crystal surfaces. The results obtained and reported here were all reproducible.

We find that there is a very close correlation between the changes in the UPS spectra and structural transitions detectable by LEED from chemisorbed acetylene on the platinum (111) surface. Both techniques reveal that chemisorbed acetylene on platinum (111) surfaces at room temperature is in a metastable state. It can be converted into a more stable state by a gentle heating to 350°K for an hour and this transformation is shown by the marked changes in the UPS difference spectra. In addition, we find that at room temperature, ethylene dehydrogenates to acetylene which is still in the disordered state on the platinum (111) surface. The incident electron beam merely
Fig. 2. Photoemission difference curve $\Delta N(E)$ for chemisorption of ethylene on the Pt(III) surface at room temperature. Work function change $\Delta \phi$ is $-0.5$ eV.
orders the already dehydrogenated species. This information cannot be obtained by LEED analysis alone since LEED studies are insensitive to the properties of adsorbates that do not exhibit long range ordering. Also, when the (2 x 2) diffraction is formed either by acetylene or ethylene adsorption, the work function change is -0.4 to -0.5 eV, indicating that approximately the same quantity of adsorbate is present on the platinum surface.

By comparison with the gas phase spectrum of acetylene molecules, we can associate the acetylene-induced emission at -3.8 and -8.2 eV (Fig. 1(a)) to the acetylene $1\pi_u$ and $3\sigma_g$ molecular orbitals respectively. Assuming uniform relaxation shifts, there is a 0.6 eV chemical bond shift for the $\pi$ orbitals due to the bonding between acetylene $\pi$ orbitals and platinum atoms on the surface in this metastable chemisorbed state. With thermally activated conversion into the stable chemisorbed state, the acetylene undergoes an apparent rehybridization, i.e., the electrons originally populated in the degenerate $\pi$ levels redistribute themselves into new levels. This is reflected by the reduction in emission of the -4.0 eV peak and the appearance of the -5.5 eV peak. The $3\sigma_g$ orbital shifts from -8.2 to -7.8 eV. This may arise from either an increased relaxation effect due to decreasing distance from the surface, or the increase of carbon-carbon distance within the acetylene molecule. The nature and degree of the indicated rehybridization in terms of surface-induced carbon-carbon bond elongation and C-C-H angle bending cannot be ascertained from the limited data available to us with the 21.2 eV photon line. We note that a transformation
very similar to the one reported herein but at a lower temperature has been studied by UPS in detail on palladium (111) by Demuth.9

In the studies reported here, we find that it is important to prepare platinum surface and the adsorbate carefully. Usually, calcium is present as a bulk impurity in platinum. On heating to elevated temperatures, the calcium may segregate to the platinum surface and cause very poor ordering of the adsorbed acetylene and probably decomposition after mild heating.10 Also, in acetylene adsorption studies, the removal of acetone appears vital in obtaining good reproducibility in UPS difference spectra for both the metastable and stable acetylene species on the platinum (111) surface.

To determine the degree of rehybridization of the adsorbates (acetylene and ethylene), it is crucial to extend the studies reported here to higher energy photon lines to probe the deeper lying orbitals. The LEED studies and accompanying dynamical calculations for beams suffering large momentum changes along the platinum surface would also be important to determine the carbon-carbon bond distance for the adsorbate.
REFERENCES


This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.