ELECTRON SPECTROSCOPY STUDIES OF CLEAN OXIDE SURFACES, CHEMISORBED MOLECULES AND PHOTO-ASSISTED PROCESSES

Wei Jen Lo
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ELECTRON SPECTROSCOPY STUDIES OF
CLEAN OXIDE SURFACES, CHEMISORBED MOLECULES
AND PHOTO-ASSISTED PROCESSES

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## ELECTRON SPECTROSCOPY STUDIES OF CLEAN OXIDE SURFACES, CHEMISORBED MOLECULES AND PHOTOASSISTED PROCESSES

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ABSTRACT

This dissertation describes the work of applying modern surface analytic techniques to characterize the surface properties of TiO\textsubscript{2} and SrTiO\textsubscript{3} that are known to possess interesting photocatalytic activities, study the chemisorption of molecules on these well-characterized surfaces and elucidate the photo-induced effects on the adsorbed molecules by the band gap illumination. Auger electron spectroscopy (AES) was employed to study the surface chemical composition whose result showed that the chemical composition of the oxide surfaces varied as a function of surface treatments. Heating at elevated temperatures, Ar ion bombardment and deposition of Ti-metal thin film resulted in an oxygen-deficient surface. Low-energy electron diffraction (LEED) showed the corresponding changes in the surface structures due to the oxygen loss. One of the most significant consequences of a derivation from stoichiometry in the surface layer is the appearance of titanium ions with unusual oxidation states. Ultraviolet photoemission spectroscopy (UPS) and electron energy loss spectroscopy (ELS) showed that on the oxygen-deficient surface there were a large concentration of Ti\textsuperscript{+3} ions which have localized d electrons. The stability of these Ti\textsuperscript{+3} oxidation states depend on surface chemical environment as well as on crystal temperature. Remarkable differences in the surface chemical composition, electronic properties and concentration of Ti\textsuperscript{+3} ions have been observed between TiO\textsubscript{2} and SrTiO\textsubscript{3} surfaces. The unique chemical properties of surface Ti\textsuperscript{+3} ions have been observed in the chemisorption studies on the well-characterized TiO\textsubscript{2} and SrTiO\textsubscript{3} surfaces. UPS and
ELS results indicated Ti$^{+3}$ is important for dissociative adsorption of chemisorbed molecules and Ti$^{+3}$ is oxidized by the adsorbed molecules. The importance of band gap illumination is to regenerate Ti$^{+3}$ after being oxidized in the presence of adsorbed molecules and to sustain the photon-assisted reaction. The photo-assisted dissociation of water into hydrogen and oxygen was investigated at solid-gas interface by AES and mass spectrometry. The chemisorption of H$_2$O, CO$_2$ and coadsorption of H$_2$O and CO$_2$ on the SrTiO$_3$ surface have been studied by UPS in order to understand the mechanism of the photon-driven thermodynamically uphill reaction of CO$_2$ and H$_2$O to form CH$_4$ which has been observed recently. Based on the experimental information of titanium oxide and strontium titanate systems, a mechanism which requires four distinct processes to take place at the active solid surface is proposed to explain the photo-assisted chemical reaction on semiconductor surfaces.
1. INTRODUCTION

Today's rapidly expanding demand for fuel in the world has exceeded the amount now available to us with existing technology. In the long run, non-exhaustible energy resources will have to be found and exploited. Among the various energy resources, such as solar, geothermal, and nuclear energy, the utilization of solar energy is the most attractive one as each year the Earth receives about $10^{25}$ Joules of energy from the Sun.\(^{[1]}\) However, solar energy suffers from the disadvantage that it is widely distributed and hence energy density at any one place is not high. One possible way to fulfil this stringent requirement for energy storage is through photochemical effects to convert solar energy directly to synthetic fuel. In principle, any endergonic chemical reaction driven uphill by light energy can represent a photochemical energy storage reaction.\(^{[2]}\) One prominent example, photosynthesis, produces hydrocarbons and oxygen from carbon dioxide and water. Recently, successful attempts to dissociate water with the assistance of light have been reported by employing reduced transition metal oxides as photoelectrodes in photoelectrochemical cells.\(^{[3-7]}\) In these circumstances, light is absorbed by a semiconductor to create energetic charge carriers of reasonable lifetime at the surface which can be used to assist the chemical reactions. This feasibility of photo-assisted chemical reaction on semiconductor surfaces opens up a new route for utilization of solar energy and will play an important role in synthetic fuel production.\(^{[8]}\)
In this study, low energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (ELS), and Ultraviolet photoemission spectroscopy (UPS) have been employed to explore the surface properties of TiO$_2$ and SrTiO$_3$ that carry out the photo-assisted chemical reactions. These oxide surfaces show detectable nonstoichiometry when heated in vacuum at elevated temperatures or after high energy (2 keV) ion bombardment. One of the most important consequences of a large deviation from stoichiometry in the surface layer is the appearance of unusual oxidation states, like Ti$^{+3}$. The stabilization of these oxidation states depends on surface environment and temperature. Marked difference in the concentration of Ti$^{+3}$ ions between TiO$_2$ and SrTiO$_3$ surfaces has been observed at room temperature. ELS, UPS, thermal desorption and work function measurement have been employed to study chemisorption of simple adsorbates on TiO$_2$ and SrTiO$_3$ surfaces. The chemisorption results indicate that Ti$^{+3}$ have very unique chemical properties and their appearance causes the dissociation of adsorbed molecules. Interaction of band gap radiation with the clean oxide surfaces and the surfaces covered with a layer of adsorbed molecules have been studied by ELS and UPS. These results reveal the photo-induced generation of active Ti$^{+3}$ ions in the surface layer and give insight about the significant role of photons in the mechanism of light-driven uphill reaction. The mass spectrometry study of photo-assisted decomposition of gas phase water molecules adsorbed onto strontium titanate surfaces is studied in the absence of liquid electrolyte.

From this study, a mechanism of the photo-assisted reaction on semiconductor surfaces is proposed which requires four distinct processes.
to take place at the active solid surface: 1) photoelectron-hole pair generation and charge separation; 2) oxidation and reduction reactions of the adsorbates and the surface with the aid of photogenerated charges; 3) rearrangement and other surface reactions of intermediates; and 4) removal of the products and regeneration of the surface.

Chapter 1: References

2. PRINCIPLES OF SURFACE ELECTRON SPECTROSCOPIES

2.1. Introduction

Surface spectroscopy in a variety of forms is now being used extensively in the study and characterization of solid surfaces. Surface spectroscopies must be selective to a rather small number of surface atoms compared to bulk atoms: a typical solid surface has $10^{15}$ atoms/cm$^2$ as compared to $10^{23}$ atoms/cm$^3$ in the bulk. The natural way to achieve this is by using particles of appropriate energy that probe only a few Å in the bulk. Among the available particles (electrons, photons, atoms, molecules and ions), electrons were found to have the widest application for a number of reasons:

1) An electron has a mean free path of a few Å with energy in the range of 10 to 1000 eV, as shown in Fig. 2.1. Electron emission from solids with energy in this range must therefore originate from the top few atomic layers.

2) Electrons are easily focused into beams and the energy can be smoothly varied by applying appropriate potentials.

3) Electrons can be efficiently detected and counted.

4) Electrons can be analyzed as a function of angle and energy using electrostatic lens and deflection systems.

5) Another major advantage of electrons as compared to atoms, molecules or ions as probing particles is that electrons do not contribute to the gas load of the vacuum system after being used for the surface analysis.

Electrons offer a wide range of different spectroscopies with different types of information: surface structure, elemental composition,
Fig. 2.1. A plot of the mean free path of electrons vs. electron energy. Note the minimum around 100 eV. The vertical line corresponds to the photon energies of various laboratory light-sources.
electronic energy distribution, and surface chemical bond. (1) The various kinds of electron spectroscopies may be divided into two subgroups: electron-excited and photon-excited spectroscopies.

2.2. Electron-Excited Spectroscopies: Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), and Electron Energy Loss Spectroscopy (ELS)

Suppose an electron beam having a well defined energy, $E_p$, is incident on a solid. The energy distribution of scattered electrons will have the form shown in Fig. 2.2. The strong peak near $E = 0$ is created by the inelastic cascade collision of incident electrons with the solid surface. The rest of the spectrum consists of three major features which turn out to be extremely useful in surface characterization.

2.2.1 The Elastic Peak: LEED

The narrow peak on the right-hand side is made of electrons which are elastically back-scattered from the solid surface without suffering any observable energy loss. The incident electron energy is usually in the range 20 to 500 eV, making the corresponding wavelength about 3 to 0.5 Å. If the surface atoms are arranged in a periodic lattice, they act as a grating for the electron waves and diffract them. Discrete electron beams will therefore appear to form a diffraction pattern that characterizes the two-dimensional periodicity of the surface, as shown in Fig. 2.3. By measuring the variation of the intensity of each diffraction spot with incident electron energy, one can, in principle, determine the location of atoms within the unit cell of the surface.
Fig. 2.2. A typical plot of the energy distribution of electrons scattered from a solid surface when a monoenergetic beam of electrons of energy $E_p$ impinges on the surface.
Fig. 2.3.
This technique for the study of surface crystallography is known as low energy electron diffraction (LEED). (2-6)

2.2.2 Auger Electron Spectroscopy

The Auger electron emission (2) is a de-excitation process for an atom that has been ionized in an inner core level. The basic mechanism of this process is illustrated in Fig. 2.4 for a K L\(_1\) L\(_{III}\) transition. A core hole in the K shell generated by the incident primary electron is filled by the electron from L\(_1\) shell. The excess energy is then transmitted radiationless to a second electron in the L\(_{III}\) shell, which then leaves the atom with a very well defined energy, \(E_k - E_{L_I} - E_{L_{III}}\) characteristic of the parent atom that emits the electron. By measuring the Auger peaks at their characteristic energies, one can therefore determine the surface elemental chemical compositions for all atoms except H. (7-10) Moreover, since the observed peak and energy of an Auger electron depends on the energy level of K, L\(_I\), and L\(_{III}\), the change in the peak shape and shift in the energy position (1-10 eV) due to the changes in the chemical environment of the parent atom can be used to determine the oxidation state of the surface atom. (9-10)

2.2.3 Electron Energy Loss Spectroscopy

These peaks are caused by energy loss of the primary incident electron in exciting the valence or core electron of the solid to a level above \(E_F\). The presence of one-electron interband transitions in ELS spectra can be interpreted by the density of states model. (11) This is illustrated by the hypothetical case for a two level system at an energy \(\Delta\) apart, with lower level occupied and upper level empty.
Fig. 2.4. Energy-level-diagram representation of the $K \text{L}_1 \text{L}_{III}$ Auger electron emission process.
The energy loss spectrum obtained for this system can be written as
\[ N(\Delta) \propto \int P_f(E) P_u(E + \Delta) dE, \]
where \( P_f(E) \) and \( P_u(E) \) are the local densities of filled and unfilled states respectively. This is shown in Fig. 2.5
where the elastic peak is shown as the one with zero energy loss and the loss peak is found at an energy \( \Delta \) below it due to one-electron transition between peaks \( P_f \) and \( P_u \). Since in the electron energy loss spectrum, both initial occupied states as well as final empty states are involved, this technique provides a unique method of characterizing both empty and filled surface electronic states. \(^{(12)}\)

In solid surfaces, the electron energy loss is not restricted to processes in which the excitation produced consists of the upward transition of a single electron as in the process shown above. Energy of an incident electron may be lost to collective motion of the electron gas of the solid (plasmons) \(^{(13)}\) and to surface atom vibration (phonons) \(^{(14,15)}\). The energy loss involved in the latter process is much smaller, viz 100 meV, as compared to the interband or collective excitation \( \sim 10 \) to 30 eV. Detection of this small energy loss requires high resolution ELS spectroscopy \(^{(1)}\) with the capability of energy monochromatization of the incident electrons and energy resolution of the emitted electrons of the order of 10 meV. In contrast to AES, this technique is capable of detecting H and determining the adsorbing sites on solid surfaces and is going to develop into a major surface analytic tool to study surface chemical bonds. \(^{(16,17)}\)
Fig. 2.5. A energy-level-diagram for a two-level system and the electron energy loss spectrum for this two-level system.
2.3. Photon-Excited Spectroscopy:
  Photoemission Spectroscopy

In electron energy loss spectroscopy, both initial filled state $P_f$ and final unfilled state $P_u$ are involved and peak in the ELS spectrum due to the one-electron transition has been interpreted as transition between peaks in $P_f$ and $P_u$. Now there is another electron spectroscopy that measures the initial filled states $P_f$ of the solid surface. Thus a combination of these two spectroscopies provides explicit information about the unoccupied as well as occupied electronic states at the surface. (18)

This spectroscopy is photon-excited electron spectroscopy, known as photoemission spectroscopy, which has emerged during the last decade as a powerful tool of directly observing occupied electronic orbitals in atoms, molecules, (19,20) solids (21) and surfaces. (1) In contrast to electron-excited spectroscopies, the photo-excited spectroscopy has very desirable features for surface study in that the photodissociation and photodesorption cross sections are very small for surface species and the surface complex usually is not affected by the measurement probe.

In photoemission experiments, monochromatic radiation of energy $h\nu$ is used to ionize the solid and the energy distribution, $N(E)$, of the emitted electrons is measured. The process involved in photoemission can be described phenomenologically as a three-step process: (22,23)

1) Electron excitation from an initial state, $|i\rangle$, to a final state, $|f\rangle$, by the absorbed photon.

2) Transport of the electron to the surface.

3) Electron escape from the surface.

The first step is analogous to an optical excitation and according to
Fermi-Golden rule is represented by the energy distribution of joint density of states (JDOS):

\[ \mathcal{D}(\epsilon, \hbar \omega) = (2\pi)^{-3} \sum_{f, i} \int' d^3 k \delta[E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar \omega] \delta[\epsilon - E_i(\mathbf{k})] |P_{fi}|^2 \]

where the prime on the integration sign denotes that \( E_i < E_F < E_f \).

The first delta function selects those transitions with energy and \( \mathbf{k} \)-conservation and the second those with a particular initial energy.

\( |P_{fi}|^2 \) is the square of the transition matrix element between initial and final states. In order to obtain an expression that may be compared with the experimental results \( N(E) \), this expression for JDOS is multiplied by a transport and escape factor \( T[E_f(\mathbf{k}), \mathbf{k}] \) to account for steps 2) and 3), i.e.,

\[ N(E) = T[E_f(\mathbf{k}), \mathbf{k}] \times \text{JDOS} \]

\[ = T[E_f(\mathbf{k}), \mathbf{k}] \times (2\pi)^{-3} \sum_{f, i} \int' d^3 k \delta[E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar \omega] \times \delta[\epsilon - E_i(\mathbf{k})] |P_{fi}|^2 . \]

Assuming constant transition matrix element, constant transport and escape, and continuum unstructured final states, then \( N(E) \) becomes

\[ N(E) = \text{constant} \times (2\pi)^{-3} \sum_{f, i} \int' d^3 k \delta[E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar \omega] \delta[\epsilon - E_i(\mathbf{k})] \]

\[ = \text{constant} \times (2\pi)^{-3} \sum_{i} \int d^3 k \delta[\epsilon - E_i(\mathbf{k})] \]

\[ = \text{constant} \times P(E) , \]
where \( P(E) = (2\pi)^{-3} \sum \int d^3k \, \delta[E - E_i(k)] \) by definition is the density of states. Thus under the above stated conditions, a photoelectron spectrum \( N(E) \) will be a direct measure of density of states.

This simple density of states concept is illustrated in Fig. 2.6 for both ultraviolet photoemission spectroscopy (He\(_I\) = 21.2 eV) and x-ray photoemission spectroscopy (Al\(_K\) = 1486.6 eV), using Si as an example. The three panels in this figure, labeled 1, 2, and 3, illustrate, respectively, the core, filled, and unfilled valence electronic states, the kinetic distribution of electrons ejected by ultraviolet radiation, and that by x-ray radiation. The shaded area in the kinetic energy distributions are due to the multiply inelastic scattered secondary electrons. Due to matrix element effects, \(^{(24)}\) XPS is more sensitive to core levels than to the valence band electrons. The influence of the chemical environment of an atom and the chemical bond is reflected in the chemical shift\(^{(1,25)}\) of the core level in XPS while with UPS these changes can be observed in the overall shape of the valence band region for a surface covered with an adsorbed layer. These changes in the valence band region may be related to the electronic structure of the surface adsorbed bond.\(^{(26,27)}\) Using a synchrotron light source, even the geometrical orientation of adsorbed molecules or atoms can be studied by the recent developments such as angle-resolved photoemission\(^{(28)}\) and extended x-ray absorption fine structure (EXAFS).\(^{(29,30)}\)
Fig. 2.6. Scheme of density of states probed by UPS and XPS.
Chapter 2: References


3. EXPERIMENTAL: A MULTIPLE-TECHNIQUE SURFACE ANALYSIS INSTRUMENT

3.1. Introduction

Each of the described electron spectroscopies has proved to be a powerful tool for surface investigations. The broadest physical and chemical information, however, is obtained by a suitable combination of several spectroscopies. In this section, descriptions of the experimental apparatus of these surface spectroscopies in the report are reviewed.

All of the experiments were performed inside an ion-pumped stainless steel ultra-high vacuum system. The ion-pump has a rated pumping speed of 1600 liters per second, and is separated from the experimental system 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. This UHV system provides a necessary and stable environment for surface cleaning and characterization study.

The instruments attached to the system can be divided into four categories: (1) Specimen manipulation and cleaning, and deposition of a thin metal film which includes the manipulator, sample holder, gas inlet manifold, ion bombardment facilities and evaporator; (2) Residual gas analysis which includes a quadrupole mass spectrometer; (3) Surface analysis, which includes LEED optics, a double-pass cylindrical mirror energy analyzer (CMA) with an internal coaxial electron gun and a HeI photon ($h\nu = 21.2$ eV) generator, capable of performing in situ LEED, AES, ELS and UPS studies on the same surface; (4) A mercury light source which provides band gap excitation in the study of photoassisted reactions.
on semiconductor surfaces. A schematic layout is shown in Fig. 3.1, various parts of which are described in the following sections.

3.2. Specimen Manipulation, Cleaning and Deposition of Thin Metal Film

3.2.1 Specimen Manipulator and Holder

The specimen manipulator (PHI model 10-504) is capable of translation in 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-wire heater mounted at the back of the crystal to facilitate the radiation heating of the crystal. The heater wire was wound non-inductively to minimize the 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 is electrically shorted to the specimen stage (made of aluminum) to avoid charging effect.

3.2.2 Ion Bombardment

For in-situ specimen cleaning, argon gas was introduced from an inlet manifold into the system through a leak to a pressure of $5 \times 10^{-5}$ torr in the experimental chamber. 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 the sample. Typical sputtering conditions were: ion energy 1~2 keV, ion beam current 10~20 microamps, beam diameter ~1.0 cm. During sputtering, the ion pump was isolated from
Fig. 3.1. The multiple-technique surface analysis system.
the experimental chamber and a titanium sublimimation pump was used to pump residual active gases outgassing from the walls of the chamber.

3.2.3 Deposition of Metal Thin Film

Deposition of a monolayer of metal thin film on the specimen surface was carried out by evaporation of the metal wire inside an evaporator which consists of a tungsten spiral filament. A stainless steel shutter, placed in front of the evaporator and operated by a rotary feed-through, was used to isolate the evaporator from the experimental chamber and to control the amount of the deposited metal. Auger signals from the deposited metal and the substrate could be monitored during evaporation.

3.3. Residual Gas Analysis

An EAI quadrupole mass spectrometer was used to monitor the residual gas composition and perform reaction product distribution and thermal desorption measurements. Under the experimental conditions, pressure changes, ΔP, on the order of 10^{-12} torr are readily detectable. For a system with pumping speed of 10 liters per sec, this corresponds to the change of particle number of 3.2 × 10^8 per sec, which is more than sufficient for most reaction and flash desorption measurements.

3.4. Surface Analysis

3.4.1 The Cylindrical Mirror Analyzer (CMA)

The essence 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 excitation source for Auger and
electron energy loss studies, and as an energy analyzer for obtaining Auger, electron loss and photoelectron energy spectra. A detailed description of its operation principle has been given by Palmberg etc. \(^{(1)}\) The CMA is superior to the retarding field grid analyzer (RFA)\(^{(2)}\) in having a very low shot noise which allows a faster energy analysis, or the use of smaller beam currents to minimize the electron beam damage on surfaces. Moreover, because of its second order focusing properties,\(^{(1,3)}\) the CMA has a very high transmission for a given energy resolution, \(~10\%\) for a single-pass CMA and \(~6\%\) for a double pass CMA with energy resolution \(<0.7\%\).

The energy resolution of the PHI 15-25G double pass CMA was measured to be 0.7%. That is, given a monoenergetic beam of electrons with energy \(E_p\), the out 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 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.\(^{(4)}\)

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 2.0 keV. Since the Auger peaks are relatively sharper than the slowly varying secondary electron background, the Auger spectrum was usually obtained in the first derivative mode to suppress the background distribution by modulating the voltage on the center cylinder of CMA 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 a retard mode to give an energy resolution of approximately 1.5 eV.

3.4.3 Electron Energy Loss Spectroscopy (ELS)

Essentially, the same experimental 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 energy monochromatization was performed, the ultimate resolution was limited by the thermal spread of the incident electrons, which was about 0.6 eV. The spectral feature was 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 $\omega$ and detecting the signal at a frequency of $2\omega$.\(^6\)
3.4.4 Ultraviolet Photoelectron Spectroscopy (UPS)

In all our photoemission studies, the HeI spectral line at 21.2 eV was used for photoexcitation. This was obtained by a d.c. cold cathode discharge of helium gas at pressure of 1 torr. Since no suitable window material exists for transmitting light of energy greater than 12 eV (cut-off energy of LiF), a windowless operation must be employed. The pressure was reduced sequentially by means of two stages of differential pumping from 1 torr in the discharge capillary, to 0.1 torr in the first stage pumped by mechanical pump, then to $1 \times 10^{-5}$ torr in the second stage pumped by diffusion pump, and finally to $1 \times 10^{-9}$ 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 the HeI 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 attached to the differential pumping manifold was used for maneuvering the photon beam to maximize the photoelectron signal.

Because of the low kinetic energy of the emitted photoelectrons (0 - 17 eV), a 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 10 eV electron beam towards the specimen and moving the specimen to maximize the elastic
Fig. 3.2. HeI (hv = 21.2 eV) photon generator.
peak. To allow the slowest photoelectrons to be collected by the CMA, a small negative (3 volts) bias was applied to the specimen in all photoemission experiments.

In typical operation, the discharge current was 150 mA and the power dissipated by the lamp was 65 watts. The photoelectron signal processing system is illustrated in Fig. 3.3. Single electron pulses are produced by a photoelectron hitting the channeltron electron multiplier. The pulses are then amplified and shaped before feeding into the discriminator. The photoelectron counts are then stored in a multichannel scaler, which can store up to four 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 placed in the optimum position. When the specimen was rotated in front of the LEED optics, this distance was such that the specimen was always slightly off-set from the center of curvature of the LEED electron optics. The LEED pattern was then slightly distorted. This problem was considered tolerable as long as the symmetry of the LEED spot pattern could be obtained.
Fig. 3.3. The pulse counting electronics system for photoemission studies.
3.5. Light Source for Band Gap Excitation

Band gap radiation was provided by a 500 watt high pressure mercury lamp in a water-cooled housing. Light from the lamp was collimated and focused on the sample with two quartz lenses. An infrared filter consisting of a quartz cell filled with NiSO₄ solution was placed in front of the lamp to absorb the heat and transmit the near UV photons. This limits the rise of temperature of specimen due to the radiation heating.

Chapter 3: References

4. PHOTOLYSIS OF H₂O ON THE TITANIUM DIOXIDE SURFACES
   BY BAND GAP PHOTONS (hν = 3 eV)

4.1. Introduction

In addition to photography, the photochemistry has found many applications in preparative organic reactions. The advantages of the photochemical method of preparing substance are either the high purity of products obtained or the low cost of their preparation and in some cases the photochemical method is the only one feasible. From the energy point of view most reactions are exergonic (ΔG < 0) and the role of light is just to overcome the activation barrier.

At the same time, endergonic (ΔG > 0) reactions are of no less interest for photochemistry both for the theory of this science and for its practical application. By carrying out an endergonic reaction driven uphill by light energy, it is possible to achieve direct conversion of the energy of solar radiation into the energy of chemical products, i.e., into the form of energy which is most convenient for storage. The photosynthesis in green plants is the well known example of this photochemical energy conversion.

Photo-induced decomposition of H₂O into hydrogen and oxygen represents another potential system for the storage of solar energy. This H₂O → H₂ + ½O₂ reaction requires a large activation energy (6.5 eV) and is not thermodynamically favorable (ΔG = +1.2 eV). However, if the required energy can be efficiently provided by light through the introduction of a solid surface (e.g., TiO₂) that lowers the activation energy, we may produce hydrogen and achieve efficient photochemical energy conversion. The feasibility of this approach has been demonstrated
using a photoelectrochemical cell where a reduced TiO₂ photoanode was employed. (3) In these solution studies, however, surface characterization has not been carried out to determine the surface structure and chemical composition of the active TiO₂ surface, thereby elucidating the mechanism of this photocatalytic reaction.

In this chapter we have carried out the studies of photo-assisted decomposition of water in the gas phase on the TiO₂ surfaces. There are many advantages for doing this. It is well known that the catalytic properties of the solid surfaces depend markedly on the surface atomic arrangement, chemical composition and electronic energy distribution. (4) Working in the gas phase at low pressure allows a direct application of modern surface analysis techniques to characterize all these properties. In the gas phase reaction, one also has a larger degree of freedom to change the surface temperature to optimize the reaction rate and to avoid the diffusion limitation of the products.

We can regard the light-induced surface chemical reaction of water dissociation as consisting of three ingredients, i.e., the semiconductor surface, the adsorbing reactant, H₂O, and photons. So the presentation of experimental results are arranged in the following order: First, I will start from the characterization of clean titanium dioxide surface. Electron spectroscopy studies show that the surface chemical composition varies as a function of surface treatments and stable metal ions with different formal oxidation states are found at the surfaces. Then I will discuss the chemisorption results of O₂, H₂O, and H₂ on these well characterized surfaces. The nature of the surface chemical bond and its relation to the surface properties of titanium oxide substrate will
be elucidated. Finally, since it is necessary to illuminate the surface by photons of band gap energy for water dissociation, the effects of light involved in the reaction are illustrated by studying the interaction of band gap radiation with a clean semiconductor surface and the surface covered with a layer of adsorbed molecules.

4.2. Characterization of the Clean (110) and (100) TiO₂ Rutile Crystal Surfaces: LEED, AES, ELS and UPS Studies

4.2.1 Selected Properties of Titanium Dioxide

Titanium dioxide can exist in three crystallographic forms, namely anatase, brookite and rutile. The rutile form of TiO₂ is the most stable form at all temperatures and both anatase and brookite transform to rutile on heating over a temperature range of 900°K to 1000°K. The rutile structure is tetragonal, with a = b = 4.59Å and c = 2.96Å (Fig. 4.1). It has the 6-3 configuration with each titanium cation surrounded by six oxygen anions at the corners of a slightly distorted octahedron while the three titanium ions coordinating each oxygen ion lie in a plane at the corners of a nearly equilateral triangle.

TiO₂ is known to be strongly ionic. One can consider the valence and conduction bands to be derived mainly from O(2p) and Ti(3d) orbitals. The bulk electronic band structure of TiO₂ has been calculated recently by Dande et al. An energy gap at 3.05 eV has been determined experimentally by the resistivity, photoconductivity, and optical absorption measurements. The dielectric constant has a high value and exhibits anisotropy; at 300°K ε₀(11₀) = 170, ε₀(11₁) = 86. The directional dependence of resistivity and mobility has also been observed.
Fig. 4.1. The titanium dioxide (rutile) crystal lattice.
The phase diagram of the O-Ti system\textsuperscript{(10)} is complicated. Below 2100°K (m.p. of TiO\textsubscript{2}), there exists at least eight intermediate titanium oxides (Ti\textsubscript{n}O\textsubscript{2n-1}, n = 3 to 10) between Ti\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}. On reduction by heating in vacuum or hydrogen at 900 K for an hour, oxygen is partially lost from the TiO\textsubscript{2} lattice and the crystal becomes blue in color. In this circumstance, conductivity measurements indicate that the crystal becomes N-type\textsuperscript{(9)} and paramagnetic resonance study shows the presence of Ti\textsuperscript{3+} species.\textsuperscript{(11,12)} The oxygen concentration can be restored by heating the reduced crystal in an oxygen atmosphere (~200 torr) at 600°C at 1 hr, as shown by the color change of the crystal from blue to yellow.

4.2.2 \textbf{Surface Structure and Composition}

Two different surfaces with (110) and (100) orientations have been studied.\textsuperscript{(13)} LEED observations in Fig. 4.2 show that the (110) surface has a stable (1\times1) structure. On the other hand, three reconstructed clean surface structures are observed on the (100) surface as shown in Fig. 4.3 by annealing the crystal at different temperatures. Annealing at 500°C results in a (1\times3) structure. Further annealing at up to 800°C gives rise to a (1\times5) structure. Finally a surface with a (1\times7) structure has been obtained with TiO\textsubscript{2} crystals are heated at 1200°C for a few minutes. Oxygen evolution has been detected by the mass spectrometer during transformation in the surface structure.

The Auger electron spectra for the clean TiO\textsubscript{2} (110)-(1\times1) surface and the same surface after Ar ion bombardment are shown in Fig. 4.4. The Auger ratio, O(510 eV)/Ti(380 eV), has dropped from 1.7 to 1.3 after Ar ion sputtering. The TiO\textsubscript{2}(100)-(1\times3) surface has the same value (1.7)
Fig. 4.2. LEED pattern from a clean ordered TiO$_2$(110) surface at an electron incident energy of 92 eV.
Fig. 4.3. LEED patterns from clean TiO$_2$(100)-(1×3), (1×5) and (1×7) surfaces. The primary electron energies are 110, 62 and 60 eV respectively.
Fig. 4.4. Auger electron spectra of (a) argon ion bombarded (b) annealed TiO$_2$(110) surface.
for the O/Ti ratio. However, this ratio decreases to 1.3 for the (1×7) surface after heating the (100) surface to 1200°C. Similar decreases in the O/T ratio has also been observed by depositing a monolayer of Ti metal on the (110) or (100) surface. (14)

4.2.3 Surface Electronic Properties

Figure 4-5 shows the results of electron energy loss spectroscopy. We see that for the TiO$_2$ (100)-(1×3) surface, there are six transitions at energies of 13.5 eV, 10.1 eV, 8.2 eV, 5.8 eV, 5.2 eV, and 2.4 eV. However, after heating the crystal to 800°C the (1×5) surface structure develops and there is an additional transition at 1.6 eV in the ELS spectrum from the (1×5) surface. Great enhancement of this 1.6 eV transition has been observed by Ar ion sputtering (13,15) or deposition of thin metal film on TiO$_2$ (100) or (110) surface. (14) This result indicates that the appearance of 1.6 eV transition accompanies the changes in surface structure and composition and thus is surface-sensitive.

Since the band gap of TiO$_2$ is 3 eV, the energies of the initial states for 1.6 eV transition have to be in the band gap region. In Fig. 4.6 we show the ultraviolet photoelectron spectra for the different TiO$_2$ surfaces. As expected, on the Ar ion bombarded surface, we find band gap emissions around -0.6 eV below the Fermi level in the photoemission spectrum. Annealing at 500°C gives an ordered (1×3) surface and results in the reduction of -0.6 eV photoelectron emissions. The corresponding change in the ELS spectrum due to heating the crystal at 500°C is the complete disappearance of the 1.6 eV transition. The close correlation between the 1.6 eV transition and the -0.6 eV photoelectron
Fig. 4.5. Electron energy loss spectra of (a) argon ion bombarded on Ti metal covered TiO$_2$(100), (b) TiO$_2$(100)-(1×3), and (c) TiO$_2$(100)-(1×5) surface.
Fig. 4.6. UPS spectra for various TiO$_2$ surfaces, obtained with $h\nu = 21.2$ eV at a resolution of 0.35 eV. All energies refer to Fermi level:

(a) argon ion bombarded (110) or (100) surface, (b) ordered (110)-(1x1) surface, (c) ordered (100)-(1x3) surface, and (d) the (100)-(1x5) surface.
emission indicates that we can assign the -0.6 eV photoelectron emission in the band gap region to be the initial occupied electronic states for a 1.6 eV transition in the ELS spectra.

In agreement with the x-ray photoemission results, we find that on the TiO$_2$(110)-(1x1) surface, the UPS spectrum shows two peaks separated by 2.7 eV in the valence band which has a band width of 6.5 eV. Ar ion sputtering causes marked changes in the shape of valence band. This result indicates the surface electronic properties are associated with surface composition, which depends strongly on surface treatments. Similar results have been obtained after depositing a thin Ti film on the (110) or (100) surface.

It is found that the work function ($\phi = h\nu$-width of the photoelectron energy distribution) decreases from 5.5 eV for the well annealed TiO$_2$(110) and (100)-(1x3) surfaces to 4.6 eV for the Ar ion bombarded surface. This monotonic decrease of work function with the surface oxygen concentration (determined by AES) can be explained by the fact that when oxygen is lost from the surface, two electrons are left in the oxygen vacancy which can easily be excited to the conduction band. This increase in the surface free-electron concentration will cause reduction of the surface dipole potential, thereby a decrease in work function.

In photo-reduced reactions, where the transport of photo-generated 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 dipole potential to allow a rapid charge transport to and away from the semiconductor surface. The ability to
change the work function and the associated dipole field by changing the surface composition after Ar ion bombardment or annealing at elevated temperature may be of importance in controlling photo-induced surface reactions.

4.3. Evidence for the Presence of Ti$^{+3}$ Species on the Oxygen-Deficient Titanium Oxide Surfaces

4.3.1 Preparation and Characterization of Oxygen-Deficient Titanium Oxide Surfaces by Heating, Ar Ion Sputtering, and Deposition of Titanium Metal

From the results of the previous section, we know that the change of surface chemical composition is a function of surface treatment. By Ar ion sputtering oxygen is removed preferentially from the TiO$_2$ surface. On annealing the sputtered surface, oxygen diffuses from the bulk to the surface thereby increasing the surface oxygen concentration and restoring the original chemical stoichiometry. However, a further increase in the annealing temperature over 800°C again causes a decrease in surface oxygen concentration and a change in surface structure because of the removal of oxygen from the lattice. Both the treatments of Ar ion bombardment and high-temperature (800°C) heating give an oxygen-reduced TiO$_2$ surface. The chemical composition of these oxygen-reduced surfaces is similar to that of non-stoichiometric titanium oxide surface covered with a thin film of titanium metal, as shown below.

In Fig. 4.7 we show the AES, ELS, and UPS spectra for the TiO$_2$(100)-(1×3) surface and the same surface covered a monolayer of titanium metal. We see that the Auger ratio $[0(510 \text{ eV})/\text{Ti}(380 \text{ eV})]$ decreases from 1.7 to 1.3 after deposition of titanium metal on the surface, indicating
Fig. 4.7. A comparison of the Auger, electron loss, and photoemission spectra of the TiO$_2$(100)-(1x3) surface before and after the deposition of one monolayer of titanium at room temperature. The spectra after Ti deposition closely resembles those of argon ion bombarded (100) surfaces.
the stoichiometry of surface chemical composition has changed. The corresponding changes in the electronic energy distribution which are associated with the changes in surface composition are reflected in the ELS and UPS spectra where new photoelectron emissions at -0.6 eV below the Fermi level are assigned to be the initial states for the 1.6 eV transition in ELS for the oxygen-reduced TiO$_2$ surfaces.

### 4.3.2 Identification of Ti$^{+3}$: Study of Oxidation of Ti Metal

Now I would like to discuss in more detail the nature of these electronic states. First of all, these states are localized near the surface, because surface spectroscopy studies reveal that their energies are located in the band gap region. Secondly, these states only appear on the oxygen-deficient surfaces. As we know, when each oxygen is lost from the surface, two electrons are left in the oxygen vacancy to maintain the charge neutrality. These electrons can be trapped by the neighboring Ti$^{+4}$ ions to form reduced titanium species, like Ti$^{+3}$.

This statement is supported by UPS and ELS studies on the Ti$_2$O$_3$ surface\(^{(15)}\) where both the 1.6 eV transition and -0.6 photoelectron emission have been observed. However, it is possible that other Ti species of lower formal oxidation states such as TiO or metallic titanium may also contribute to these emissions. In order to prove that Ti$^{+3}$ is the only species responsible for these omissions, we have studied the oxidation of titanium single crystal metal and monitored the intensity of 1.6 eV transitions in ELS as a function of oxidation states of Ti.\(^{(14)}\)

The specimen used was a 99.99% single crystal of titanium metal. The Ti(0001) surface, as determined by the Lane back-reflection technique was cut from the crystal and mechanically polished using 1.0 μm Al$_2$O$_3$. 
powder. The titanium sample was held in place by two spot-welded foil contacts through which the current was passed to facilitate direct heating of the titanium sample. Gross impurities on the surface were first removed by Ar ion bombardment. Then the crystal was heated at 300-500°C in an oxygen flow mode, with local oxygen pressure \( \sim 10^{-5} \) torr to remove residual carbon on the surface and sulfur 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 (1×1) surface.

The oxidation was performed at a substrate temperature of 573°K and at oxygen pressure of \( 10^{-7} \) to \( 10^{-6} \) torr. The chemical composition of oxides formed on the Ti metal surface was monitored by measuring the Auger peak ratio, \( O(510 \text{ eV})/Ti(380 \text{ eV}) \), and studying the details of the Ti Auger peak shape changes at 410 eV which accompany the changes in the Ti oxidation state. The \( O(510 \text{ eV})/Ti(380 \text{ eV}) \) ratio reached a constant value of 1.1 at an oxygen exposure of \( 10^3 \)L or greater. By comparing the AES peak shapes and ELS spectrum with those from the stoichiometric TiO\(_2\)(100)-(1×3) surface, we conclude that the top layer of titanium metal was oxidized all the way to titanium dioxide, TiO\(_2\), as has been found by previous photoemission studies.\(^{(17)}\) The fact that the O/Ti Auger ratio (1.1) is less than that on the TiO\(_2\)(100)-(1×3) surface (1.7) indicates that not all of the titanium atoms have been oxidized within the electron mean free path (\( \sim 10 \) Å). We estimate that an oxide of thickness about 6 Å has formed, which then acts as a diffusion barrier against further oxidation. This is supported by the constancy of the \( O(510 \text{ eV})/Ti(380 \text{ eV}) \) Auger peak ratio with further oxygen exposure up to \( 10^5 \)L.
In Fig. 4.8 we show the intensity of the 1.6 eV ELS transition as a function of the O/Ti atomic ratio, the latter being obtained from the O(510 eV)/Ti(380 eV) Auger peak ratio. We assume that an O(510 eV)/Ti (380 eV) Auger peak ratio of 1.1 on the fully oxidized Ti metal surface corresponds to an O/Ti atomic ratio of 2. This calculation yields values of an O/Ti atomic ratio which agrees very well with that obtained by AES and LEED intensity analysis.\textsuperscript{(18)} The 1.6 eV ELS transition acquires a sharp maximum at an O/Ti ratio of 1.5 and falls off rapidly to either side of the maximum. The O/Ti atomic ratio of 1.5 corresponds to a chemical composition of Ti\textsubscript{2}O\textsubscript{3}. Because the -0.6 eV emissions in UPS are the initial states for the 1.6 eV ELS transition, both emissions, can be used to monitor the existence of Ti\textsuperscript{4+} on the oxygen-reduced TiO\textsubscript{2} surfaces.

4.4. Electron Spectroscopy Studies of Chemisorption of O\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O on the TiO\textsubscript{2} Surfaces with Varied Stoichiometry: Importance of Ti\textsuperscript{4+} in Chemisorption

4.4.1 Introduction

In this section, I would like to show the results of chemisorption of O\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O on the titanium oxide surfaces.\textsuperscript{(14)} From the studies of surface characterization, we know that we can prepare stable surface metal ions with different formal oxidation states (e.g., Ti\textsuperscript{4+} via Ti\textsuperscript{4+}). Because of the appearance of localized d electron in the metal ion (3d in Ti\textsuperscript{4+}), we expect it will exhibit very interesting chemical activities. This is reflected in the results of electron spectroscopy and thermal desorption studies which show strong dependence of surface chemical bonding on the formal oxidation states of titanium ions for chemisorption.
Fig. 4.8. The intensity of the 1.6 eV ELS transition as a function of O/Ti atomic ratio.
4.4.2 Results

4.4.2.1 UPS studies of chemisorption of O\textsubscript{2} on the TiO\textsubscript{2} surfaces.

The UPS spectra N(E) for clean TiO\textsubscript{2}(100)-(1x3) surface and for the same surface after exposure to 10\textsuperscript{5} L oxygen at room temperature are shown in Fig. 4.9. The photoemitted electron energies were measured relative to E\textsubscript{F}. Three new emissions appeared after oxygen adsorption which were located at -5.2 eV, -6.8 eV, and -10.3 eV respectively. The work function, determined by measuring the width of the photoemission curves, was found to increase +0.2 eV. We note in Fig. 4.9 that there is a parallel shift of valence band edge emission toward E\textsubscript{F}. This suggests that the work function increase induced by oxygen adsorption is accompanied by the change of upward band bending in the space charge region near the surface.

The UPS spectrum of Ar ion sputtered TiO\textsubscript{2}(100) surface is shown in Fig. 4.10. The characteristic -0.6 eV emission in UPS indicates it is an Ti\textsuperscript{4+3} rich surface. After exposing this surface to 10\textsuperscript{5} L oxygen, the same three oxygen-induced emissions appear in the UPS spectrum as on the oxygen-rich surface, as shown in Fig. 4.10. The intensity of the -0.6 eV emission from the surface was reduced after oxygen adsorption. The work function change, $\Delta \phi$, in this case was +0.3 eV and the same shift of valence-band edge emission has occurred.

4.4.2.2 UPS studies of chemisorption of H\textsubscript{2} on the TiO\textsubscript{2} surface.

The results of hydrogen adsorption on TiO\textsubscript{2}(100)-(1x3) surfaces and Ar ion sputtered surfaces are presented in terms of photoemission difference curves, $\Delta N(E)$, and are shown in Fig. 4.11. They were obtained after subtraction of the UPS spectra N(E) for the clean substrate surface from
Fig. 4.9. Photoemission distribution curves $N(E)$ of the TiO$_2$(100)-(1×3) surfaces before and after $10^5$ L oxygen exposure at room temperature.
Argon bombarded TiO$_2$

$D\phi = +0.3$ eV
$T = 300^\circ$K

Electron Binding Energy, eV

Fig. 4.10. Photoemission distribution curves $N(E)$ of the Ar ion bombarded TiO$_2$(100) surfaces before and after $10^5$ L oxygen exposure at room temperature.
Fig. 4.11. Photoemission difference curve $\Delta N(E)$ of TiO$_2$ (100)-(1×3) surface and Ar ion bombarded surface after $10^5$ L hydrogen exposure at room temperature.
those for the surfaces after hydrogen adsorption. The surfaces were exposed to $10^5$ L hydrogen at room temperature. The hydrogen adsorbed on the TiO$_2$(100)-(1x3) surface induced three emission peaks in $\Delta N(E)$ located at -5.5 eV, -7.7 eV, and -10.8 eV, respectively. The work function change was -0.4 eV. The adsorption of hydrogen on the Ar ion sputtered surface showed a different $\Delta N(E)$ which had emission peaks at energies of -4.3 eV, -7.6 eV, and -10.0 eV. The work function change was +0.1 eV. Thus there is a reverse sign of work function change $\Delta \phi$ for hydrogen adsorption on the oxygen-rich surface and Ti$^{+3}$-rich surface.

4.4.2.3 UPS studies of chemisorption of H$_2$O on the TiO$_2$ surfaces.

Figure 4.12 shows the UPS spectra $N(E)$ for the TiO$_2$(100)-(1x3) surface before and after exposure to $10^5$ L H$_2$O at room temperature. The adsorbed H$_2$O induced three distinct new emissions which are superposed on the emissions from the clean TiO$_2$(100)-(1x3) substrate surface. These three peaks are located at -6.1 eV, -7.8 eV, and -11.2 eV. The work function of the sample decreased from 5.7 eV to 4.9 eV after H$_2$O adsorption. LEED showed that the (1x3) pattern became diffuse and the background intensity increased. This indicated that H$_2$O adsorbed on TiO$_2$(100)-(1x3) surfaces in a disordered manner.

After heating the TiO$_2$(100)-(1x3) sample above 800°C for two hours, the (1x7) surface structure appeared and the O/Ti Auger ratio drops from 1.7 on the (1x3) sample to 1.4. The UPS spectra of the clean TiO$_2$(100)-(1x7) surface and with chemisorbed H$_2$O on this surface are shown in Fig. 4.13.

The appearance of the -0.6 eV emission in the UPS spectrum of clean TiO$_2$(100)-(1x7) surfaces indicated the presence of detectable amounts of
Fig. 4.12. Photoemission distribution curves $N(E)$ of TiO$_2$(100)-(1×3) surface before and after $10^5$ L H$_2$O exposure at room temperature in the dark.
Fig. 4.13. Photoemission distribution curves $N(E)$ of TiO$_2$(100)-(1x7) surfaces before and after $10^5$ L H$_2$O exposure at room temperature in the dark.
Ti$^{+3}$ species on this surface. After exposing the (1x7) surface to $10^5$L H$_2$O at room temperature, the UPS spectrum for this surface showed the appearance of four new emissions which are located at -4.8, -6.3, -7.9, and -10.8 eV, respectively, relative to E.F. The intensity of the -0.6 eV emission in the UPS spectrum of the (1x7) surface after H$_2$O adsorption was found to be reduced. The accompanying work function change was -0.4 eV.

After chemisorption of H$_2$O on the Ti deposited TiO$_2$(100) surface using $10^5$L exposure at room temperature, we obtained an adsorbed water UPS spectrum which was different from those obtained for the (1x3) and (1x7) surfaces. Part (c) and (d) of Fig. 4.14 shows the photoemission distribution curve N(E) after H$_2$O chemisorption on the Ti-deposited surface and its difference curve $\Delta$N(E) after subtracting the emission from the substrate surface. Three new emissions appear as a result of H$_2$O chemisorption on this Ti-deposited Ti$^{+3}$-rich surface. The positions of these three peaks are -4.2, -7.5, and -10.4 eV, respectively. In part (c) of Fig. 4.14 we found that the intensity of -0.6 eV emission in the UPS spectrum is smaller compared to that in part (b). The work function change after H$_2$O adsorption in this case was -0.1 eV. The identical UPS spectra was obtained for H$_2$O adsorption on an Ar ion sputtered surface as shown in Fig. 4.15.

In Fig. 4.16 we plot the photoemission difference curves for chemisorption of H$_2$O on TiO$_2$(100)-(1x3), -(1x7), and Ti-deposited (or Ar ion sputtered) surfaces. By changing the surface chemical composition which was indicated from the decrease of values of the Auger O/Ti ratio, we observe changes in the shape and energy positions of water-induced
Fig. 4.14. UPS spectra of (a) clean TiO$_2$(100)-(1x3) surface, (b) Ti-deposited surface, and (c) the surface with adsorbed water layer; (d) shows the photoemission difference curve $\Delta N(E)$: (c)-(b).
Fig. 4.15. UPS spectra of Ar sputtered TiO$_2$(100) surface before and after $10^5$ L H$_2$O exposure at room temperature.
Fig. 4.16. Photoemission difference curves of water adsorbed on three different titanium oxide surfaces. The chemical composition of each surface is indicated by the Auger O(510eV)/Ti(380eV) ratio. The dotted line is UPS spectrum of gas phase water.
emissions in the difference curves $\Delta N(E)$. The gas phase $H_2O$ photoemission spectrum was also included for comparison in Fig. 4.16.

4.4.2.4 Thermal desorption studies of $H_2O$ on the $TiO_2$ surfaces.

Thermal desorption measurements were carried out after room temperature exposure of $10^5$ L $H_2O$ to $TiO_2(100)$ surfaces of varying stoichiometry. The oxygen-to-titanium ratio was varied by Ar ion sputtering and annealing in vacuum or in an oxygen atmosphere, typically of $10^{-5}$ torr. The specimen was indirectly heated by passing a current of 20 A through a Ta heater foil which holds the crystal. The heating rate of the specimen was not a constant; it was 2.5°C/sec at 150°C and 1°C/sec at 250°C. A quadrupole mass spectrometer, directly facing the sample, was set at $m/e = 18$ to detect $H_2O$ desorbed from the surfaces. Blank experiments showed that the amounts of $H_2O$ desorbed from the Ta foil were extremely small and could be differentiated easily.

Figure 4.17 shows a series of such thermal desorption profiles of water ($m/e = 18$). On the oxygen-rich titanium oxide surface (top-most curve in Fig. 4.17), there are two distinct peaks at ~150 and 230 C. As the $O/Ti$ ratio is decreased (which means a simultaneous increase in the surface $Ti^{+3}$ concentration, as evidenced by ELS and UPS), the 230 C peak shifts slightly to higher temperature and dominates over the 150 C peak. At an $O(510 eV)/Ti(380 eV)$ Auger ratio of 1.3, the thermal desorption profile shows a dominant peak at 250 C and a weak shoulder at 150 C.

4.4.3 Discussion

The UPS spectrum of a $TiO_2(100)-(1\times3)$ surface after oxygen adsorption shows three new emissions with energies of -5.2, -6.8, and -10.3 eV.
Fig. 4.17. Thermal desorption profiles of water adsorbed on titanium oxide surfaces of different stoichiometries.
Since the previous studies\(^\text{(13)}\) show the -10.3 eV peak occurs only for a disordered TiO\(_2\) surface, the appearance of this emission after oxygen adsorption on the TiO\(_2\)(100)-(1×3) surface indicates the adsorbed oxygen forms a disordered overlayer. This is consistent with LEED observations which show the (1×3) pattern degraded after oxygen adsorption.

The adsorption of oxygen on the Ar sputtered oxygen-deficient surface gives rise to the same three oxygen-induced emission in the UPS spectrum. The decrease in intensity of the -0.6 eV emission near the Fermi edge shown in Fig. 4.10 indicates the removal of surface Ti\(^{+3}\) species by adsorbed oxygen from the surface. Both work function increase and shift of valence band edge emission toward \(E_F\) in UPS were found on TiO\(_2\)(100)-(1×3) and Ar sputtered TiO\(_2\)(100) surfaces after oxygen adsorption. Since adsorbed oxygen is an electron acceptor it increases the upward band bending in the space charge region near the TiO\(_2\)(100) surface, thus causing this effect.

In contrast to oxygen adsorption, UPS studies show that the adsorption of hydrogen on the TiO\(_2\)(100)-(1×3) surface was different from that on the Ar ion bombarded surface. The \(\Delta N(E)\) spectra shown in Fig. 4.11 has emissions with different energy positions for hydrogen adsorption on these two surfaces having different chemical compositions. The work function change after hydrogen adsorption reverses sign for these two surfaces. These results indicate that the adsorbed hydrogen forms surface chemical bonds to the TiO\(_2\)(100)-(1×3) surface which are different from that of the Ar ion sputtered surface. On the clean TiO\(_2\)(100)-(1×3) oxygen-rich surface, there are only Ti\(^{+4}\) ions. The adsorbed hydrogen behaves like an electron donor. By preferential
removal of surface oxygen during Ar ion bombardment, there is a large increase in the surface concentration of Ti\(^{+3}\). Adsorbed hydrogen becomes an electron acceptor on the surface. The appearance of Ti\(^{+3}\) species caused major changes in the bonding of adsorbed hydrogen molecules which are reflected in the variation of UPS \(\Delta N(E)\) spectra and the reversal of the sign of the work function change.

Chemisorption of water has been studied by UPS on three different types of clean titanium oxide(100) surfaces: [1] the (100)-(1\times3) surface, which has no detectable concentration of Ti\(^{+3}\); [2] the (100)-(1\times7) surface, which has a small concentration of surface Ti\(^{+3}\) present; [3] Ti-deposited (or ion sputtered) TiO\(_2\)(100) surfaces which have large amounts of Ti\(^{+3}\) present. The photoemission difference curves for each titanium oxide surface are shown in Fig. 4.16. The difference curve of adsorbed water on TiO\(_2\)(100)-(1\times3) surface compares very closely with the photoemission spectrum of gas-phase molecular water. By aligning the -11.2 eV emission in the difference curve with the 1\(b_2\) molecular orbital of water, we obtain a relaxation shift of 2.1 eV. The energy separation between -11.2 eV and -7.8 eV emissions in \(N(E)\) is identical to the energy difference between 1\(b_2\) and 3\(\sigma_1\) orbitals of molecular water. The -6.1 eV emission was assigned to the 1\(b_1\) orbital which suffers an additional shift of -0.5 eV toward larger binding energy, probably as a result of chemical bonding to the substrate surface. The similarity of this difference curve to the UPS spectrum of gas phase water is strong evidence that water is adsorbed as an intact molecule on the (1\times3) Ti\(^{+3}\)-free TiO\(_2\) surface.

On the (1\times7) surface, which is still ordered, there appears a
detectable amount of Ti$^{+3}$ species, as shown in Fig. 4.13. The photoemission difference curve for adsorbed water on the (1x7) surface shows distinctly different features from that for the adsorbed water on TiO$_2$(100)-(1x3) surface. There are four peaks in $\Delta N(E)$ rather than three for molecular water. The three lower-lying peaks are shifted slightly (0.1 to 0.4 eV) with respect to the corresponding peaks on the (1x3) surface. A new peak develops at -4.8 eV. This suggests that part, if not all, of the adsorbed water is either decomposed or bound to the surface differently in the presence of Ti$^{+3}$ at the surface.

Further reduction of the surface oxygen concentration by Ar ion sputtering (or Ti deposition) of the surface results in a Ti$^{+3}$-rich surface as indicated by the dominant 1.6 eV transition in the ELS spectrum in Fig. 4.7 and the enhancement of the Fermi-edge -0.6 eV emission in UPS (see Figs. 4.14 and 4.15). While the adsorbed water on this oxygen-deficient surface shows a three-peak UPS $\Delta N(E)$ spectrum, this $\Delta N(E)$ spectrum is completely different from the photoemission difference curve of adsorbed water on the (1x3) oxygen-rich surface. The -4.8 eV peak continues shifting to -4.2 eV, the -6.1 eV peak disappears, and the -11.2 eV peak moves up to -10.1 eV with less binding energy.

Due to the distinct differences between this $\Delta N(E)$ spectrum and the gas phase water UPS spectrum, we propose a model where the adsorbate is not molecular water but a different chemical species such as a hydroxyl group. This is supported by the observation that the adsorbed hydrogen and water on Ti$^{+3}$-rich surfaces both have very similar photoemission difference curves as shown in Figs. 4.11 and 4.16. If we assume that the hydrogen molecule is adsorbed dissociatively on the Ti$^{+3}$-rich surface,
then due to the presence of oxygen on the titanium oxide lattice, the hydrogen atoms will form surface hydroxyl groups which have a photo-emission spectrum as in Fig. 4.11. This ΔN(E) UPS spectrum is consistent with the gas phase photoemission spectrum of OH(20) which shows two ionization potentials (relative to vacuum level) of 13.01 eV and 15.20 eV respectively. The additional -4.3 eV emission in ΔN(E) suggests that the surface hydroxyl group on the surface may be (OH)− due to the charge transfer between the adsorbate and the substrate surface. This UPS result is consistent with theoretical calculation(21) of chemisorption of water on the rutile surface.

The results of flash desorption showed the corresponding changes in the thermal desorption curves of water which were adsorbed on the different surfaces with varying chemical compositions. For Ti4+3-rich surfaces, the desorption peak of water dominates at 250 C while the 150 C peak is developing with the increase in oxygen concentration at the surface. These results, which were obtained on well characterized surfaces in the UNV chamber, were consistent with the infrared spectroscopy studies(22-26) of water adsorption on TiO2 powders, which showed that the lower temperature desorption peak (at 150 C) is due to chemisorbed molecular water and that the higher temperature peak (at 250 C) corresponds to water resulting from the condensation of surface hydroxyl groups. Results of electron simulated desorption measurements(27) also suggest that water is either dissociated when adsorbed on the Ar sputtered TiO2 surface into hydroxyl groups, or is in a metastable state which dissociates easily.
Combining all the results from UPS, thermal desorption, electron beam stimulated desorption, and infrared spectroscopy studies, we conclude that on the stoichiometric TiO$_2$ surface, water adsorbs associatively, whereas on the oxygen-deficient Ti$^{+3}$-rich surface (by Ar ion bombardment or deposition of Ti metal), the adsorbed water tends to dissociate into surface hydroxyl groups. The strong interaction between the adsorbed water and surface Ti$^{+3}$ species is evidenced by the 100 C increase in thermal desorption temperature and results in the oxidation of Ti$^{+3}$ to Ti$^{+4}$. The corresponding phenomena$^{(28)}$ are seen in solution where Ti$^{+3}$ ions are shown to be strong reducing agents reacting with H$_2$O to form Ti(OH)$_2^+$. The progressive changes of UPS spectra in Fig. 4.16 indicate the degree of dissociation of adsorbed water depending on the concentration of Ti$^{+3}$ species on the surface.

After water adsorption in the dark, the change of work function $\Delta\phi$ is -0.8 eV for the TiO$_2$(100)-(1x3) surface and -0.1 eV for the Ar ion sputtered surface. This indicates adsorbed water is an electron donor and causes a large change in the surface dipole potential. This decrease of surface dipole potential and its associated electric field may cause the increase of electron-hole recombination rates in the space charge region near the surface during light illumination and hence reduce the number of energetic free charge carriers that reach the surface contributing to the reaction. This might explain why an additional external voltage, which increases the surface electric field, is necessary to start the water dissociation reaction in the electrochemical cell.$^{(3)}$ From the studies of oxygen adsorption, we know that the chemisorption of gases (e.g., O$_2$, N$_2$, etc) with large electronegativities
results in an increase of surface electric field. This suggests the co-adsorption of these kinds of gases with water vapor during light illumination might also increase the reaction rate.

4.5. Effects of Band Gap Illumination: Photogeneration of Ti$^{+3}$

4.5.1 Introduction

According to the electronic theory of catalysis on semiconductors\(^{(29,30)}\), mobile charge carriers at the surface (electrons or holes) can interact with adsorbed molecules and can participate in surface reactions. Absorption of photons of band gap energy by a semiconductor induces band-to-band electron transition, where a hole and an electron are photo-produced and this leads to a change in the concentration of electrons and holes on the surface, which affects the surface reactivity.

There are two classes of reactions that can occur as the photo-produced holes and electrons reach the surface. The first is simple recombination with no chemical change in the system. The second class of reaction is photocatalysis, where electrons and holes are captured by different surface groups:

\[
\begin{align*}
\hbar \nu + e^- & \rightarrow h^+ \\
e^- + X^{n+1} & \rightarrow X^n \\
h^+ + M^m & \rightarrow M^{m+1} \\
X^{n+1} + M^m & \xrightarrow{\hbar \nu} M^{m+1} + X^n
\end{align*}
\]

where the $\hbar \nu$ in the above equation indicates a photo-induced reaction. Generally, a photo-induced reaction may have many steps. In both cases holes and electrons have been recombined. However, in the first class,
the photon energy has been dissipated finally as heat, while in the second class, the photon energy has been used to cause a chemical reaction to take place which could not otherwise have occurred because of an activation energy. In the case of photochemical conversion, some of the photon energy is actually converted to chemical energy.

All the experimental results that I have discussed so far were performed in the dark. Since it is necessary to illuminate the surface in the water-dissociation reaction, in the next section I would like to show the effects of light on this reaction. The UV light source for band gap radiation comes from a high pressure mercury lamp.

4.5.2 Effects of Band Gap (3 eV) Illumination on the TiO$_2$(100)-(1×3) Surface: Photo-induced Generation of Ti$^{+3}$ Species

The TiO$_2$(100)-(1×3) surface was prepared by Ar ion sputtering and subsequent annealing at 500°C. LEED observation showed well defined integral and fractional order diffraction spots. To make sure that the electron beam used in our LEED studies did not induce any significant reduction of titanium dioxide surface, the crystal was annealed again at 500°C after taking the LEED pattern. An energy loss spectrum was then taken using a 20 to 40 eV electron beam to avoid electron beam-induced energy loss transition. This procedure is sufficient to generate a well ordered TiO$_2$(100)-(1×3) surface with no detectable Ti$^{+3}$ present.

After the surface was illuminated at room temperature with a focused beam of UV light for periods ranging from 20 min to 1 hour, no change could be observed in UPS and AES. However, after 25 min exposure the (1×3) surface to the UV light exhibited a shoulder at 1.6 eV which could clearly be seen in the ELS spectrum (Fig. 4.18). The possible
Fig. 4.18. The energy loss spectra of the TiO$_2$(100)-(1×3) surface (a) before and (b) after 25 mins UV illumination. Light intensity (hv ≥ 3 eV) is $10^{17}$ cm$^{-2}$ sec$^{-1}$. Primary energy of the incident electron beam is 20 eV.
reducing effect of 20 eV electron beam can be ruled out. In order to generate the 1.6 eV transition with the intensity shown in Fig. 4.18 without UV light requires at least 20 min continuous electron beam exposure, while the total time required to take the two spectra shown in Fig. 4.18 is less than 30 sec.

The experiment was also carried out by exposing the surface to UV light at crystal temperature ranging from 323K to 473K. No 1.6 eV transition could be observed in the ELS spectrum after one hour irradiation. This result excludes the possibility of thermal generation of Ti$^{+3}$ during light illumination and can be explained in terms of increase of surface oxygen concentration with elevated temperature by diffusion of bulk oxygen that removes the photo-generated Ti$^{+3}$ species.

4.5.3 Effects of Light on Water Adsorbed on the Ar Ion Sputtered Ti$^{+3}$-rich Surfaces

The Ti$^{+3}$-rich titanium oxide surface was prepared by Ar ion bombardment of TiO$_2$(100)-(1×3) surface with a 2 keV, 10 μA argon ion beam for $10^3$ sec. The presence of Ti$^{+3}$ species was detected by UPS, which showed the Fermi-edge emission at -0.6 eV.

The photoemission curves for the surface covered with adsorbed water before and after UV light illumination are shown in Fig. 4.19. By comparing these two figures, we notice two distinctly different features as a result of illumination. First, in contrast to the case of water adsorption in the dark, where reduction in the intensity of -0.6 eV photoelectron emission was observed, there is almost no decrease in the intensity of this emission from the same water-covered surface after UV light illumination. This observation is consistent with the
Fig. 4.19. UPS spectra of the clean Ar ion bombarded TiO$_2$(100) surface and the same surface after $3 \times 10^3$ L H$_2$O exposure and $10^4$ sec UV light illumination at room temperature.
ELS result which provides firm evidence for the photogeneration of Ti$^{+3}$ by band gap radiation. Second, we find work function increases from 4.4 eV to 4.8 eV during light illumination of the water-covered surface, while the adsorption of water in the dark on the same surface causes work function decrease, $\Delta \phi = -0.1$ eV. The difference in the work function change before and after light illumination on the surface covered with a water layer implies light may induce change in the nature of chemisorbed water species.

4.5.4 Discussion

From these observations, the role of light in the photoassisted decomposition of water on the titanium oxide surface becomes clear. UPS studies show that surface Ti$^{+3}$ species are the active sites for the initial water dissociation into surface hydroxyl groups. However, this process is quickly poisoned in the dark since Ti$^{+3}$ is oxidized by reacting with the adsorbed molecules. Band gap radiation is needed to regenerate Ti$^{+3}$ active sites and sustain the reaction.

4.6. Conclusion

In this study we find that surface treatments of high temperature heating (over 1100 K), Ar ion bombardment and deposition of titanium metal can reduce surface oxygen concentration and decrease surface dipole potential ($\Delta \phi = -1.0$ eV). Electron spectroscopy studies provide firm evidence for the existence of Ti$^{+3}$ species on the oxygen reduced surface. Since all the samples used in the photoelectrochemical cell$^3$ have been reduced to have an oxygen-deficient surface, the presence of surface Ti$^{+3}$
and the associated change in surface dipole potential during the sample preparation play very important roles in determining the surface photocatalytic activities. The Ti$^{+3}$ surface concentration is reduced by adsorption of O$_2$ and H$_2$O or by heating in the temperature range of 323K to 473K, while it can be restored by photons of band gap energy.

Water adsorbs associatively on the stoichiometric TiO$_2$ surface while it appears to dissociate and form OH$^-$ on the Ti$^{+3}$-rich surface. The thermal desorption spectra indicate that in the presence of Ti$^{+3}$, the adsorbed water is bound more strongly to the surface. The adsorbed water is an electron donor which decreases the surface dipole potential, while adsorbed oxygen is an electron acceptor which increases the surface dipole potential.

From these observations a physical picture of the photon-assisted dissociation of water on the titanium oxide surface begins to emerge. It appears that a reduced Ti$^{+3}$-rich monolayer forms on top of a TiO$_2$ surface that is stable under illumination (in fact, it can be photo-generated) and plays an important role in the dissociation of water molecules. We may view the active surface as a surface compound since further reduction of the TiO$_2$ bulk is controlled by slow ion diffusion processes. Ti$_2$O$_3$ has metallic conductivity and in the absence of a stable surface space charge it is not active in the photon-assisted reaction (since it may provide rapid recombination paths for photogenerated electrons and holes). Stoichiometric TiO$_2$ is not active in decomposing water since it lacks sites for the initial dissociative adsorption process. However, in combination with an active monolayer on top of a substrate of large surface dipole potential, it provides a suitable catalyst for this photon-assisted reaction.
Chapter 4: References

5. TEMPERATURE-DEPENDENCE SURFACE STRUCTURE, COMPOSITION, AND ELECTRONIC PROPERTIES OF THE CLEAN SrTiO$_3$(111) CRYSTAL FACE: LOW-ENERGY-ELECTRON DIFFRACTION, AUGER-ELECTRON SPECTROSCOPY, ELECTRON ENERGY LOSS, AND ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY STUDIES

5.1. Introduction

In addition to TiO$_2$, strontium titanate (SrTiO$_3$) is one of the few other stable materials that can decompose water into hydrogen and oxygen with the assistance of light of band gap energy (3.2 eV at 25°C) or greater in the photoelectrochemical cell.\(^1\) The photoelectrolysis can be sustained using SrTiO$_3$ as an anode (where oxygen evolves) and platinum as a cathode (hydrogen evolution), without the use of an external potential. This may be contrasted with the TiO$_2$ photoanode\(^2\) that requires +0.2 volt external potential to carry out the same photo-assisted water dissociation reaction in the same experimental configuration.

In addition to possessing this remarkable photocatalytic property, strontium titanate has interesting semiconducting, superconducting, and optical properties. Stoichiometric SrTiO$_3$ is an insulator transparent to visible light. At room temperature, it is cubic but undergoes a transition to a tetragonal structure at about 110K.\(^3\) When strontium titanate is reduced, it takes on a blue color and becomes semiconducting. Strontium titanate displays a number of interesting photochromic and electrochromic properties\(^4\) when doped with metal ions and hence has potentially important electro-optic applications in areas such as image storage, photochromism, and electrochromism. Doped strontium titanate is also a superconductor\(^5\) with a transition temperature of about 0.3K. The atomic structure and electronic properties of bulk strontium titanate
crystal have been thoroughly studied both by theory and by experiments. Theoretical calculations of the bulk band structure of SrTiO$_3$ have been reported by Kahn et al.$^{(6)}$ and Matheiss$^{(7)}$ and are in fairly good agreement with the results of photoemission experiments by Shirley et al.$^{(8)}$ Compared to the data that have been accumulated on the bulk properties, the surface structure and electron energy distribution of the SrTiO$_3$ surface are relatively unexplored. Walfram et al.$^{(9)}$ have carried out theoretical surface energy band calculation of strontium titanate which suggests the existence of a highly localized d-electron surface band in the band-gap region and emphasizes its importance in surface chemical reactions. Experiments$^{(10,11)}$ have been performed only recently that investigate the SrTiO$_3$ surface electron distribution, using ultraviolet photoelectron spectroscopy (UPS).

Since the catalytic properties of surfaces depend strongly on their atomic surface structure, chemical composition and electronic distribution, it is important to investigate all of these properties. In this chapter a combination of surface analysis techniques has been employed to characterize the clean strontium titanate single crystal face with (111) orientation. Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to study the surface structure and chemical composition, respectively. Electron energy distributions were studied by energy loss spectroscopy (ELS), and ultraviolet photoemission spectroscopy (UPS). It is found that for SrTiO$_3$, the crystal temperature plays an important role in determining its surface structure, chemical composition, and electronic distribution. By comparing the surface properties of TiO$_2$ and SrTiO$_3$, we attempt to explain the difference
in the photoactivity observed when these materials were utilized in the photoelectrochemical cell.

5.2. Specimen Preparation and Cleaning

The specimen used was a 99.99% undoped strontium titanate single crystal with perovskite structure. Two samples of (111) orientation, as determined by the Lane back reflection technique, were cut from this crystal and mechanically polished using 0.05 μm Al₂O₃ powders. The specimen was then rinsed in distilled water and mounted on a high density alumina holder, which had a tungsten heater wire located at the back of the sample to allow radiative heating of the crystal.

The in-situ cleaning of the SrTiO₃ surface was attained by Ar ion bombardment of the surface at a pressure of 6 × 10⁻⁵ torr argon gas. With an accelerating voltage of 2 keV, an argon beam of typically 20 μA could be delivered to the sample surface.

5.3. Results

5.3.1 LEED and AES Studies of the Surface Structure and Chemical Composition of Clean SrTiO₃(111) Surface as a Function of Temperature

The LEED pattern obtained from the SrTiO₃(111) surface at room temperature is shown in Fig. 5.1. The surface exhibits a stable (1×1) surface structure after Ar ion bombardment at 27°C to remove impurities, then annealing at 600°C for 30 min. However, after Ar ion bombarding at 600°C, the surface seems to facet as indicated by the LEED pattern (Fig. 5.2), and the surface assumes a complex structure. The (1×1) surface structure can be restored after removal of the faceted surface
Fig. 5.1. Low-energy electron diffraction patterns of the clean SrTiO$_3$(111) surface after Ar ion bombardment at 27°C and subsequent annealing at 600°C. (A) $E_p = 24$ eV, (B) $E_p = 32$ eV.
Fig. 5.2. Low-energy electron diffraction patterns of the clean SrTiO$_3$(111) surface after Ar ion bombardment at 600°C and subsequent annealing at 600°C. (A) $E_p = 25$ eV, (B) $E_p = 34$ eV.
by extended Ar ion bombardment (20 min) at 27°C followed by annealing at 600°C for 20 min.

The Auger electron spectrum for the clean SrTiO$_3$(111)-(1×1) surface at 27°C is shown in Fig. 5.3. The value of the Auger peak-to-peak ratios of Sr(65 eV)/O(510 eV) and O(510 eV)/Ti(380 eV) in the AES spectrum for this surface are 1.5 and 2.0, respectively. Figure 5.4 shows the AES spectrum from the SrTiO$_3$(111) surface at a temperature of 600°C. By comparing with the AES spectrum in Fig. 5.3 we find the shape of titanium Auger peak at 416 eV has changed and the Auger Sr(65 eV)/O(510 eV) ratio drops to 1.1. The emission from the hot filament of the heater prevented LEED observation of SrTiO$_3$(111) surface at 600°C. After cooling the crystal to 27°C, the AES spectrum returned to that shown in Fig. 5.3 and LEED showed a (1×1) surface structure at 27°C. This heating and cooling cycle has been repeated several times and the above results are quite reproducible. It appears that the surface concentration of strontium becomes less with increasing temperature in a reversible manner.

Figure 5.5 shows the AES spectrum of the clean SrTiO$_3$(111) surface after ion bombardment at 27°C. The detailed feature of the Auger titanium and oxygen peaks in this AES spectrum are very similar to those of Ar ion sputtered TiO$_2$ surface.$^{(12)}$ While there is only little change in the value of the Auger O(510eV)/Ti(380eV) ratio upon ion bombardment, the Sr(65eV)/O(510eV) peak ratio shows a remarkable increase from 1.5 (for (1×1) surface) to 2.8 (for Ar ion bombarded surface at 27°C). It appears that Ar ion bombardment at 27°C removes oxygen preferentially from the surface region.
Fig. 5.3. Auger electron spectrum of the clean ordered SrTiO$_3$(111)-(1x1) surface at 27°C.
Fig. 5.4. Auger electron spectrum of the clean ordered SrTiO$_3$(111) surface at a temperature of 600°C.
Fig. 5.5. Auger electron spectrum of the clean room temperature argon ion bombarded SrTiO$_3$ surface. The AES spectrum taken at 27°C.
The AES spectra of the SrTiO$_3$(111) surfaces which were Ar ion bombarded at 27°C and 600°C, respectively, are shown in Fig. 5.6. Both spectra were taken at 27°C after the same 2 keV Ar ion dosage to the surface. Comparison of these spectra exhibits two distinct differences. First, we find that the shapes of titanium Auger peaks in the AES spectra are different. For the room temperature ion bombarded SrTiO$_3$ surface, the shape of the Auger titanium peak at 416 eV resembles that of the same peak in the Ar ion sputtered TiO$_2$ surface. The shape of the corresponding titanium peak for the SrTiO$_3$ surface after ion sputtering at 600°C resembles that of the same peak in the well annealed TiO$_2$ surface. Second, the value of the Auger Sr(65eV)/O(510eV) ratio is higher for the SrTiO$_3$ surface after high-temperature (600°C) ion sputtering. It increases from 2.8 (for ion sputtering at 27°C) to 4.1 (for ion sputtering at 600°C). It appears that high-temperature argon ion-bombardment induces a large enrichment of strontium in the SrTiO$_3$ surface.

5.3.2 ELS and UPS Studies of Electron Energy Distribution at the Clean SrTiO$_3$(111) Surface as a Function of Temperature

5.3.2.1 Electron energy loss spectroscopy.

The energy loss spectra for the clean SrTiO$_3$(111) crystal faces obtained after the different surface treatments are shown in Fig. 5.7. In Fig. 5.7(a) the ELS spectrum of the clean SrTiO$_3$ surface is shown after Ar ion bombardment at 27 C. There are six distinct transitions: at 13.1, 10.3, 7.7, 5.6, 3.1, and 1.6 eV. The gross features of this spectrum are very similar to those reported for the Ar ion sputtered TiO$_2$(12) surfaces, except on the SrTiO$_3$ surface there is one more transition at 7.7 eV. Both TiO$_2$ and SrTiO$_3$ surfaces show a distinct 1.6 eV transition
Fig. 5.6. AES spectra of (a) room temperature, (b) high temperature (600°C) Ar ion bombarded SrTiO$_3$ surfaces. Both spectra were taken at room temperature.
Fig. 5.7. Electron energy loss spectra of the clean SrTiO₃ (111) surface at temperatures of (a) 27°C, (b) 300°C, (c) 500°C, (d) 600°C, (e) 300°C, (f) 27°C, after room temperature Ar ion bombardment. The LEED pattern from the surface that corresponds to (f) indicates an ordered (1×1) surface structure.
after Ar ion sputtering at 27°C that is associated with the presence of Ti$^{3+}$ ions at the surface.\(^{(13,14)}\) The ELS spectrum obtained at 300°C upon annealing the crystal at this temperature is shown in Fig. 5.7(b). The intensity of 10.3 eV transition has increased while the intensity of 7.7 eV has decreased. There is also an observable reduction in the intensity of the 1.6 eV transition. Figures 5.7(c) and 5.7(d) show the ELS spectra for the same SrTiO$_3$ crystal surface at 500°C and 600°C, respectively. We find that there is a continuous reduction of the intensity of the 1.6 eV transition that is associated with the presence of Ti$^{3+}$ and it finally disappears at 600°C. After cooling the crystal back to 300°C, the 1.6 eV transition reappears as shown in Fig. 5.7(e). Successive cooling of the crystal back to room temperature results in an ELS spectrum as shown in Fig. 5.7(f). In comparison with that in Fig. 5.7(e), the intensity of the 1.6 eV transition in Fig. 5.7(f) is enhanced. The LEED pattern from the surface that yields the ELS spectrum of Fig. 5.7(f) indicates the presence of an ordered (1×1) surface structure. The heating and cooling cycles have been repeated several times and the results are very reproducible. Thus it appears that the composition and electronic energy distribution of the SrTiO$_3$ surface changes reversibly with surface temperature.

In Fig. 5.8 we show the ELS spectra for the SrTiO$_3$ surfaces that were Ar ion bombarded at 27°C and 600°C, respectively. Both surfaces have the same Ar ion dosages and the spectra were obtained when the crystal reached room temperature after sputtering. Although the relative peak intensities of the 13.1, 10.3, 5.6, and 3.1 eV transitions are similar in the two ELS spectra, the intensity of the 7.7 eV transition
Fig. 5.8. Electron energy loss spectra of the clean SrTiO$_3$(111) surfaces (a) after room temperature Ar ion bombardment, (b) after high temperature (600°C) Ar ion bombardment. Both spectra were taken at room temperature of 27°C.
is higher in Fig. 5.8(b). In addition, while there is a distinct 1.6 eV transition in the ELS spectrum for the SrTiO$_3$ surface after Ar ion bombardment at 27°C, this transition completely disappears from the ELS spectrum for the SrTiO$_3$ surface after high-temperature (600°C) Ar ion sputtering.

5.3.2.2 Ultraviolet photoelectron spectroscopy.

The UPS spectrum for the Ar ion sputtered surface at 27°C is shown in Fig. 5.9. In agreement with the work of Henrich,\(^{(11)}\) an emission at -0.6 eV below the Fermi level $E_F$ in the band gap region is observed. This is consistent with the result obtained for Ar ion bombarded TiO$_2$ surfaces,\(^{(12,13)}\) which show the same -0.6 eV emission in the UPS spectra. This emission is associated with the presence of Ti$^{3+}$ in the oxide surfaces.\(^{(13,14)}\) In Fig. 5.9 there are also other emission peaks with energies at -2.6 eV, -6.0 eV, and -10.8 eV, respectively. The work function $\phi$ of this surface is 3.4 eV.

Subsequent annealing at 600°C resulted in the disappearance of the -10.8 eV and -2.6 eV emissions and splitting of the broad -6.0 eV peak into two emissions with energies at -6.9 and -4.8 eV respectively, as shown in Fig. 5.10. We also find that the intensity of the -0.6 eV emission in the band gap region has been reduced. However, this emission always has a detectable intensity at 27°C, even after annealing the crystal at 800°C for two hours. The LEED pattern which corresponds to the UPS spectrum shown in Fig. 5.10 indicates that the surface has a (1x1) structure. The work function of this clean ordered SrTiO$_3$(111)-(1x1) surface is 5.2 eV.

The temperature dependent changes in the UPS spectra for the
Fig. 5.9. The UPS spectrum of the Ar ion bombarded clean SrTiO$_3$ surface at 27°C.
Fig. 5.10. The UPS spectrum of the clean, ordered SrTiO$_3$(111)-$(1\times1)$ surface. The spectrum was taken at a temperature of 27°C.
clean, ordered SrTiO$_3$(111) surfaces are shown in Fig. 5.11 which display the curves taken at 27°C, 300°C, and 600°C. There is a continuous reduction in the intensity of the -0.6 eV emission with increasing crystal temperature. This change is reversible — after cooling the SrTiO$_3$ crystal to room temperature, the same initial UPS spectrum is obtained.

Figure 5.12 shows the UPS spectrum from the clean SrTiO$_3$(111) surface after Ar ion bombardment at 600°C. This spectrum was taken at a crystal temperature of 27°C after the high-temperature sputtering process. In contrast to the room temperature Ar ion bombarded SrTiO$_3$ surface, we find the Fermi edge emission at -0.6 eV has disappeared almost completely. The work function of this surface is 4.0 eV.

5.4. Discussion and Comparisons of Surface Properties of SrTiO$_3$ and TiO$_2$ Crystals

The change in the strontium to oxygen Auger peak ratio and the constancy of the oxygen to titanium ratio indicates oxygen and titanium are removed preferentially from the SrTiO$_3$(111) surface by Ar ion sputtering at room temperature. On annealing this sputtered surface, strontium diffuses into the bulk, thereby decreasing the strontium concentration on the surface. The chemical composition of the SrTiO$_3$(111) surface can be varied reversibly by changing the crystal temperature, as shown by AES. Although similar temperature-dependent surface composition has been observed for binary alloy surfaces, our result is the first report of this effect for a ternary oxide compound.

Auger electron spectroscopy analysis also shows that the crystal temperature during Ar-ion sputtering can cause marked changes in the chemical composition of the SrTiO$_3$(111) surface. After a high-temperature
Fig. 5.11. The UPS spectra of the clean, ordered SrTiO$_3$(111) surfaces taken at temperatures of 27°C, 300°C and 600°C, respectively.
Fig. 5.12. The UPS spectrum of the high-temperature (600°C) Ar ion sputtered SrTiO$_3$(111) surface. The spectrum was taken at 27°C.
(600°C) Ar ion sputtering treatment, there is a remarkable increase in the strontium concentration and annealing does not alter this surface composition any more. The room temperature Ar ion bombarded SrTiO$_3$ surface has a lower strontium surface concentration and its value is decreased after annealing at 600°C. This indicates that high-temperature Ar ion bombardment yields a stable Sr-rich phase on the SrTiO$_3$(111) surface, which behaves differently from the room temperature Ar ion sputtered SrTiO$_3$ surface. LEED studies also indicate structural differences between the two surfaces that were ion bombarded at 27°C and 600°C, respectively, after annealing.

The electron energy distributions of the SrTiO$_3$(111) surface as a function of surface treatments are studied by ELS and UPS. The transition peaks at 13.1, 10.3, 7.7, and 5.5 eV in the ELS spectra have also been observed by M. Cordova$^{(16)}$ using the ultraviolet reflectance technique. The bulk states which are involved in these transitions have been assigned.$^{(16)}$ The ultraviolet photoemitted electrons from the SrTiO$_3$ surface come from two sources: from the states in the valence band and from states in the band gap region. While AES shows oxygen loss from the SrTiO$_3$ surface as a result of argon ion sputtering at 27°C, the ELS spectrum of the Ar ion-sputtered SrTiO$_3$ surfaces shows a strong peak at 1.6 eV. Since the band gap of SrTiO$_3$ is 3.2 eV, the initial states of the 1.6 eV transition must be located in the band gap region. Indeed, a band gap emission at -0.6 eV in the UPS spectrum was found in this sputtered SrTiO$_3$ surface and was assigned to be the initial states for the 1.6 eV transition. In agreement with the results for the TiO$_2$ surfaces,$^{(12-14)}$ these 1.6 eV transition and -0.6 eV emission are characteristic of the
of the presence of surface $\text{Ti}^{3+}$ species. In contrast to the case of the $\text{TiO}_2$ surface, where annealing caused the complete disappearance of $\text{Ti}^{3+}$ species, the $\text{SrTiO}_3(111)-(1\times1)$ ordered surface after annealing always has detectable amounts of $\text{Ti}^{3+}$ present at room temperature.

The UPS spectrum of $\text{SrTiO}_3(111)-(1\times1)$ shows that the width of the valence band is 6.5 eV and two major emission peaks separated by 2.1 eV are resolved. This result is consistent with the recent XPS studies of Shirley et al.,\(^{(8)}\) and gives a reasonable fit to the density of state calculations of Mattheiss.\(^{(7)}\) The difference in the shapes of valence bands in the UPS spectra between the room temperature Ar ion-sputtered $\text{SrTiO}_3$ surface and the $\text{SrTiO}_3(111)-(1\times1)$ surface is due to the change in surface stoichiometry that is induced by Ar ion sputtering. In addition, the UPS spectrum of the $\text{SrTiO}_3$ surface after Ar ion sputtering at 27°C shows the presence of occupied states with energies around -2.6 eV which are located right above the valence band maximum. The absence of these states on the $\text{SrTiO}_3(111)-(1\times1)$ surface after annealing indicates that they are extrinsic surface states induced by Ar ion sputtering at 27°C.

The reversible variation of the intensity of the -0.6 eV UPS emission and 1.6 eV ELS transition of $\text{SrTiO}_3$ surface as a function of temperature reveals that the concentration of surface $\text{Ti}^{3+}$ species depends on the crystal temperature. At 27°C, there is a large concentration of $\text{Ti}^{3+}$ species ($\sim 10^{14}/\text{cm}^2$) on the ordered surface. Raising the crystal 300°C, the reduction of $\text{Ti}^{3+}$ concentration is observed and a complete disappearance of $\text{Ti}^{3+}$ species is obtained by heating the crystal above 600°C. However, subsequent cooling of the crystal to room temperature
results in the reappearance of the surface Ti$^{3+}$ species. The combination of our ELS, UPS, and AES studies indicates that the temperature of the ternary oxide crystal controls its surface stoichiometry which in turn determines many of the surface electronic properties. The persistent difference in the surface Ti$^{3+}$ species concentration between the TiO$_2$ and SrTiO$_3$ surfaces at room temperature indicates that excess Sr stabilizes the formation of Ti$^{3+}$.

The combination of ELS, UPS, AES, and LEED studies indicates that high-temperature (600 C) Ar ion sputtering treatment causes an irreversible change in the surface structure, surface chemical composition and electronic properties and yields a stable strontium-rich phase.

The different surface treatments of the SrTiO$_3$ surface result in a drastic change of the work function and hence a large change in the surface dipole potential. In photo-assisted reactions on the semiconductor surface where the transport of photo-generated charge carriers at the surface is the rate-determining step, it is desirable to increase the electric field near the surface to allow a rapid charge transfer to and from the surface. In the case of TiO$_2$, Ar ion sputtering produces a large concentration of Ti$^{3+}$ species and a marked decrease in the surface dipole potential. Subsequent annealing increases the work function and the associated surface dipole potential, but removes all the Ti$^{3+}$ species on the surface. However, in the case of SrTiO$_3$ surfaces, where annealing also causes the increase of the work function, Ti$^{3+}$ ions are always present at room temperature after annealing. Since the presence of surface Ti$^{3+}$ species aids the dissociation of adsorbed water, an active Ti$^{3+}$ monolayer on top of a substrate with large surface dipole
potential provides a suitable catalyst for this photo-assisted reaction. The important differences in surface composition and work function shown in Fig. 5.13 appear to be the cause of the differences in photo-activity between TiO$_2$ and SrTiO$_3$ that are used in the photo-electrochemical cell.\(^{1,2}\)

5.5. Conclusion

Using LEED, AES, ELS and UPS, we have characterized the surface structure composition and electronic distribution of the (111) single crystal surface of SrTiO$_3$. The dependence of the surface chemical composition on the temperature has been observed along with corresponding changes in the surface electronic properties. High temperature Ar ion bombardment causes an irreversible change in the surface structure, stoichiometry and associated electron energy distribution. In contrast to the TiO$_2$ surface, there are always significant concentrations of Ti$^{3+}$ species on the SrTiO$_3$ surface which also has a larger surface dipole potential. The stable, active Ti$^{3+}$ monolayer on top of a substrate with large surface dipole potential makes SrTiO$_3$ superior to TiO$_2$ when used as a photoanode in the photoelectrochemical cell.
Fig. 5.13. The electron energy loss spectra and the corresponding work functions of: (a) clean, ordered SrTiO$_3$(111)-(1×1) surface, (b) ordered TiO$_2$(100)-(1×3) surface, and (c) the clean Ar ion sputtered TiO$_2$ surface. Notice the persistent appearance of 1.6 eV transition on the SrTiO$_3$(111)-(1×1) surface which has also a larger work function than that of the Ar sputtered TiO$_2$ surface. All ELS spectra were taken at room temperature.
References: Chapter 5

6. THE PHOTO-ASSISTED DECOMPOSITION OF GAS PHASE WATER ADSORBED ON SrTiO₃

6.1. Introduction

In this chapter we report on the photo-assisted decomposition of water molecules from the gas phase to hydrogen and oxygen when adsorbed on polycrystalline strontium titanate surfaces. This occurs without applying an external potential and in the absence of any liquid electrolyte. This is the first observation of this process using vapor phase water in which radiation of energy less than the dissociation energy of water (~5.2 eV) has been used.

Ever since the report of photo-assisted decomposition of liquid water by Fujishima and Honda, (1) there has been much work on the photo-assisted production of hydrogen and oxygen, mostly in aqueous solutions using various semiconductor photoelectrodes that were immersed in electrolytes. (2-12) In some of these systems for efficient generation of hydrogen at the metal counter-electrode and oxygen at the illuminated semiconductor photoanode a small external potential (less than the necessary 1.23 volts for water) had to be applied, in others none at all. In all cases, photons of energy greater than or equal to the band gap of the semiconductor electrode have to be used to initiate and sustain the decomposition of water.

There are many advantages in carrying out the photon assisted decomposition of water in the vapor phase over solid-liquid (electrochemical cell) systems. Working in the gas phase at low pressures (less than 10⁻⁶ torr) allows the direct application of the various analytical tools of modern surface science to monitor the composition, structure,
and electronic states of the surface during the reaction and to identify the nature and oxidation states of both the substrate and the adsorbate. The reaction mechanisms can then be uncovered and understood more clearly this way. One may also be able to change the surface temperature over a broader range to optimize the production rates of hydrogen and oxygen without concern for the absorption of light by the electrolyte or diffusion limitation of the products.

6.2. Experimental

Our experiments of the photon-assisted decomposition of water vapor were performed inside a multiple-technique ultrahigh vacuum chamber with a base pressure less than $1 \times 10^{-10}$ torr, as was used in our previous characterization studies of titanium dioxide surfaces. It consists of an ion-pumped stainless steel UHV system, equipped with LEED, Auger and UPS capabilities for surface analysis and a quadrupole mass spectrometer for gas analysis. Strontium titanate powders of 99.95% purity were obtained from Electronic Space Products, Inc., of Los Angeles. The powders were compressed into 7/8-inch diameter pellets. Two such samples were made. One of them was reduced by heating to 1200°C at a hydrogen pressure of one atmosphere for an hour and this showed a slightly greyish color after reduction. The external surface area for both samples was approximately $2.5 \times 10^3 \text{ cm}^2$. Both samples (reduced and unreduced) were immersed into distilled water and then removed to dry. Each powder sample was then mounted on a 1.5 x 1.5 inch square platinum foil backing and held in place by two spot-welded platinum wires. The arrangement was such that either sample could be illuminated without illuminating
the other. Auger electron spectra from the samples that were obtained in the UHV chamber showed carbon as the principle surface impurity. The carbon concentration corresponded to approximately 0.5 monolayer.

Band gap radiation was provided by a 500 watt high pressure mercury lamp which was water and air cooled during maximum power operation. The UV light generated was transmitted to the specimen through a sapphire window, shown in Fig. 6.1. 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 directly. An infrared filter, made from filling a quartz cell with nickel sulfate solution, was placed between the mercury UV source and the focusing lens to absorb the heat and transmit the near UV. This limits the rise in temperature of the specimen due to radiation heating to less than +30 °C and hence avoids any spurious effects due to thermal desorption. The total photon flux on the sample was estimated to be ~10^{17} photons (energy >3 eV) per second, as measured by a calibrated Eppley pyroheliometer. To increase the detection sensitivity, the ion pump was throttled to give effective pumping speeds of 2, 20, and 70 liters/sec for water, oxygen, and hydrogen, respectively. The approximate wavelength response was checked by inserting various glass filters and measuring the photo-induced mass spectrometer signal. The energy threshold for the production of H_2 and O_2 was thus determined to be 3.5±0.5 eV. This agrees well with the band gap of SrTiO_3 (3.2 eV).
Fig. 6.1. Experimental arrangement for studying photo-decomposition of water on SrTiO$_3$ surfaces.
6.3. Results and Discussion

The difference plots of Fig. 6.2 show that by shining UV light onto the strontium titanate samples held at room temperature, the partial pressures of $\text{H}_2$ ($m/e = 2$), $\text{H}_2\text{O}$ ($m/e = 18$), and oxygen ($m/e = 32$) were found to increase instantaneously to a steady level. This pressure increase was practically constant over a period of an hour or more, and occurred only when the light was incident on the sample. After converting ion difference currents to pressures and correcting for pumping speed differences, the number of molecules leaving the semiconductor surface per second is plotted in Fig. 6.3. The reduced sample appears to evolve more hydrogen and oxygen when illuminated. Photodesorption of molecular water ($m/e = 18$) was also observed. However, the amounts of $\text{H}_2$ and $\text{O}_2$ detected are at least two orders of magnitude greater than could be accounted for by the fragmentation of the photodesorbed water in the mass spectrometer.

The experiment was repeated by coabsorbing $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ onto the same SrTiO$_3$ surfaces at a pressure of $10^{-6}$ torr for 20 minutes. After evacuating the system to $\sim 2 \times 10^{-10}$ torr the samples were illuminated with UV light. In addition to the evolution of $\text{H}_2$ ($m/e = 2$), $\text{H}_2\text{O}$ ($m/e = 18$), $\text{D}_2\text{O}$ ($m/e = 20$), and $\text{O}_2$ ($m/e = 32$), both HD ($m/e = 3$) and $\text{D}_2$ ($m/e = 4$) were detected. Again, the reduced sample always gave larger photo-induced signals than the unreduced sample. In both experiments it was found that only light with energy greater than $\sim 3$ eV is effective in giving rise to all the observed increases in mass spectrometer signals.

Several important observations can be immediately extracted from the above experimental results. First, the ratio of the number of
Fig. 6.2. Increase of the mass spectrometer ion currents ($\Delta I$) over the signals obtained in the dark as a result of UV illumination on water adsorbed on strontium titanate powder surfaces.
Fig. 6.3. Rates of hydrogen, water and oxygen evolution due to UV illumination on water adsorbed on strontium titanate powder surfaces.
hydrogen molecules to that of oxygen leaving the semiconductor surface is approximately 40 to 1 for the reduced SrTiO₃ sample, and 140 to 1 for the unreduced one. While these numbers are uncertain to a factor of 2, the ratios are still far from the stoichiometric ratio of 2:1 as expected from the decomposition of water. Since the Auger spectra show surface carbon impurities, the depletion of oxygen by the following reactions:

\[
\begin{align*}
\text{C(surface)} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO(gas)} \\
\text{CO(surface)} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2(gas) \\
\text{C(surface)} + 2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{CO}_2 \\
2\text{C(surface)} + 2\text{H}_2\text{O} & \rightarrow \text{CH}_4 + \text{CO}_2
\end{align*}
\]

is very likely. These possibilities are supported by the observation of increased ion current at m/e = 28 (ΔI = 1.3 × 10⁻¹⁰ A) and m/e = 44 (ΔI = 4.5 × 10⁻¹⁰ A), upon illumination of the surface. The magnitude of the increase in partial pressures of CO and CO₂ are more than sufficient to explain the discrepancy in the H₂/O₂ ratio. We note that among the possible reactions to produce CO₂, reactions (3) and (4) have positive free energy changes of 0.65 eV/mole and 0.2 eV/mole respectively, as shown in Fig. 6.4. The occurrence of these two reactions apparently need to be photocatalyzed. Similar observation of CO₂ production during UV light illumination upon a ZnO surface was found by Shapiro et al.\(^{(15)}\) Quantitative determination of CO₂ production from each reaction is not possible at present. Future studies using single crystal surfaces will allow us to verify this point. Another possibility is the intermediate formation of hydrogen peroxide which is only partially decomposed on the
\[
\begin{align*}
C \text{(graphite)} + 2 \text{H}_2\text{O (g)} &= 2 \text{H}_2 + \text{CO}_2 & \Delta G^\circ &= 0.65 \\
2 \text{C (graphite)} + 2 \text{H}_2\text{O(g)} &= \text{CH}_4(g) + \text{CO}_2(g) & \Delta G^\circ &= 0.12
\end{align*}
\]

Fig. 6.4. Free energy changes for reactions between carbon and water to form H\textsubscript{2} and CH\textsubscript{4}.  

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on the surface. Indeed, small quantities of hydrogen peroxide were detected in the electrochemical cells using \( \text{SrTiO}_4 \) as a photoanode.\(^6\)

Second, the reduced \( \text{SrTiO}_3 \) sample is at least 20% more efficient than the unreduced sample in the photoassisted decomposition of adsorbed water. This may be related to differences in charge carrier mobilities in the two samples. Preliminary experiments on \( \text{SrTiO}_3 \) single crystals show that lower oxidation state titanium species (vis. \( \text{Ti}^{3+} \)) are present in higher concentrations in partially reduced \( \text{SrTiO}_3 \). The presence of \( \text{Ti}^{3+} \) species may substantially enhance the reaction rate.\(^{14}\) Also, the evolution of HD when the \( \text{SrTiO}_3 \) sample, with a coadsorbed layer of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), is illuminated by band gap radiation implies that at least one of the OH bonds in water is broken on adsorption to the \( \text{SrTiO}_3 \) surface. Similar behavior has been found for water adsorbed on reduced titanium dioxide surfaces.\(^{13}\) Finally and perhaps most significantly, the \( \text{D}_2\text{O} \) experiment clearly demonstrates that the observed hydrogen evolution is due to water decomposition and not simply to photodesorption.

The successful photoassisted decomposition of adsorbed water vapor opens up a new area of investigation of photoassisted thermodynamically uphill processes on semiconductor surfaces. This result is especially encouraging since they indicate that other photoassisted but thermochemically forbidden oxidation-reduction reactions\(^{16,17}\) will also be feasible.
Chapter 6: References

17. J.C. Hemminger, R. Carr, and G.A. Somorjai, to be published.
7. ELECTRON SPECTROSCOPY STUDIES OF CHEMISORPTION OF \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{CO} \), \( \text{CO}_2 \), AND \( \text{H}_2 \) ON THE \( \text{SrTiO}_3 \) SINGLE CRYSTAL SURFACE: PHOTO-INDUCED EFFECTS ON CHEMISORBED MOLECULES

7.1. Introduction

We have embarked on a program to explore the possibility of carrying photo-assisted catalytic reactions at the solid-vapor phase that are thermodynamically uphill, i.e., accompanied by a large positive free energy change.

In Chapter 6, we reported the photo-assisted decomposition of water molecules from the gas phase to hydrogen and oxygen when adsorbed on polycrystalline strontium titanate surfaces. Recently, observation of the possibility of producing methane from the photosynthetic reaction of water and carbon dioxide molecules on the clean single crystal \( \text{SrTiO}_3(111) \) surface has been reported.\(^{(1)} \) The use of well characterized single crystal surfaces instead of the use of higher surface area powders makes the surface easy to clean and avoids the possible side reactions due to contaminants, mainly carbon.

There are advantages in carrying out chemical reactions other than the dissociation of water. Although thermodynamically uphill, the reactions of \( \text{CO}_2 \) and water in producing a variety of hydrocarbons (methane or methanol, for example) require less energy input per electron transferred (have lower \( \Delta E^0 \) values) than that needed to dissociate water.

\[
\begin{align*}
\text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \rightarrow \text{CH}_4(g) + 2\text{O}_2(g) \quad , \quad \Delta E^0 = 1.037 \text{ eV} \\
\text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \rightarrow \text{CH}_3\text{OH}(g) + 3/2\text{O}_2(g) \quad , \quad \Delta E^0 = 1.19 \text{ eV} \\
\text{H}_2\text{O}(g) & \rightarrow \text{H}_2(g) + 1/2\text{O}_2(g) \quad , \quad \Delta E^0 = 1.23 \text{ eV} 
\end{align*}
\]
In general, the photon-assisted reaction requires four distinct processes to take place at the active solid surface:

1) photoelectron-hole pair generation by light, charge separation and trapping,
2) oxidation and reduction reactions of the adsorbates with the aid of the photogenerated charges,
3) rearrangement and other surface reactions of intermediates,
4) removal of the products and regeneration of the surface.

In order to understand the reaction mechanisms of the complex photo-reaction of methane formation from CO\(_2\) and H\(_2\)O, we have started from the study of chemisorption of CO\(_2\), H\(_2\)O, H\(_2\), O\(_2\) and CO on the various SrTiO\(_3\) crystal surfaces in the dark and in light by ultraviolet photoemission spectroscopy. These studies reveal that the nature of the adsorbed species are closely related to the surface chemical composition and the associated electronic energy distribution and show the significant roles light has played in the reaction.

7.2. Chemisorption of O\(_2\) on the SrTiO\(_3\) Surfaces in the Dark and the Effect of Band Gap UV Light Illumination on Chemisorbed Oxygen

When oxygen is introduced into the vacuum chamber at pressure of 10\(^{-6}\) torr, adsorption on the oxide surface takes place. Typical exposures were about 10\(^n\) Langmuir. The UPS spectra, N(E), which reveal three oxygen-induced photoelectron emissions at -10.6 eV, -6.6 eV, and -4.6 eV after oxygen chemisorption on the SrTiO\(_3\)(111)-(1×1) surface, are shown in Fig. 7.1. The work function is increased by \(\Delta\Phi = +0.9\) eV, and the Ti\(^{+3}\) signal is completely removed by chemisorbed oxygen. Illumination
Fig. 7.1. UPS N(E) spectra for O$_2$ adsorbed on SrTiO$_3$ (111)-(1×1) surface, before and after illumination.
of the surface with band gap radiation after oxygen adsorption regenerates a significant amount of surface Ti$^{+5}$, as shown in Fig. 7.1. However, upon illumination of the oxygen covered surface, the work function is reduced by only 0.2 eV, which is still 0.7 eV greater than the work function of the clean (1×1) surface and the oxygen-induced emissions still remain. The facts that the work function does not return to the value of the clean surface and that there is still oxygen-induced emissions in the UPS spectrum upon illumination indicate that not all the adsorbed oxygen is removed by photodesorption. We also notice in Fig. 7.1 that there is a parallel shift of +0.5 eV in the valence band edge, indicating an increase in work function accompanying the change in band bending.

Figure 7.2 shows the UPS spectra for the clean Ar ion sputtered SrTiO$_3$ surface and the same surface after oxygen adsorption. The same three oxygen-induced photoelectron emissions are found and the Ti$^{+3}$ signal is completely removed after oxygen adsorption. The work function change $\Delta\Phi$ is +0.9 eV and the same shift of valence band edge emission has occurred. Illumination of the oxygen-covered surface with band-gap radiation restores a significant amount of Ti$^{+3}$ but does not remove all the chemisorbed oxygen, as shown in Fig. 7.2.

7.3. Chemisorption of H$_2$O, H$_2$ on the SrTiO$_3$ Surfaces in the Dark and the Effect of Band Gap UV Light Illumination on the Adsorbed Water

The UPS spectra for the clean SrTiO$_3$ (111)-(1×1) surface and the same surface after $5 \times 10^4$ L H$_2$O adsorption are shown in Fig. 7.3. Three water-induced photoelectron emissions whose energies are located at
Fig. 7.2. UPS N(E) spectra for $O_2$ adsorbed on Ar ion bombarded (at 27 C) SrTiO$_3$ surface, before and after illumination.
Fig. 7.3. UPS N(E) spectra for H$_2$O adsorbed on SrTiO$_3$(111)-(1×1) surface, before and after illumination.
-10.6, -6.6, and -4.1 eV are observed. The signal due to the presence of Ti$^{+3}$ ions decreases upon H$_2$O absorption, indicating much of the Ti$^{+3}$ is oxidized to Ti$^{+4}$ by the adsorbed water molecule. The work function is found to increase which may be due to the change in surface dipole potential as a result of water adsorption. This is in striking contrast to water adsorption on TiO$_2$ which causes a decrease in the work function of -0.8 eV.(2)

When water adsorption is followed by illumination of the surface with band gap radiation, the Ti$^{+3}$ signal is partially restored, as shown in Fig. 7.3. The work function is not affected.

Figure 7.4 shows the clean room temperature Ar ion bombarded SrTiO$_3$ surface and the same surface after $9 \times 10^3$ L H$_2$O adsorption. There are three water-induced photoelectron emissions with energies at -10.6, -6.0, and -4.5 eV respectively. The decrease in Ti$^{+3}$ signal after H$_2$O adsorption indicates that the adsorbed water oxidizes Ti$^{+3}$ to Ti$^{+4}$. The work function is found to increase +0.4 eV after H$_2$O adsorption.

Figure 7.5 shows the UPS spectra of the high temperature (600°C) Ar ion bombarded surface and the water-covered surface after $9 \times 10^3$ L H$_2$O adsorption. The absence of -0.6 eV photoelectron emissions in Fig. 7.5(a) indicates there is no Ti$^{+3}$ present at the surface after high temperature Ar ion bombardment.(3) This Ti$^{+3}$-free surface provides a unique substrate to study the chemisorption of water as a function of Ti$^{+3}$ concentration at the SrTiO$_3$ surface. In contrast to the chemisorption of H$_2$O on the room temperature Ar ion bombarded surface (i.e., Ti$^{+3}$-rich surface), where there are three water-induced emissions at -10.6 eV, -6.6 eV, and -4.1 eV chemisorption of H$_2$O on the high temperature Ar ion
Fig. 7.4. UPS N(E) spectra of the Ar ion sputtered (at 27 C) SrTiO$_3$ surface before and after a H$_2$O exposure of 9 x 10$^3$ L at room temperature.
Fig. 7.5. UPS N(E) spectra of the Ar ion sputtered (at 600°C) SrTiO₃ surface before and after a H₂O exposure of 9 x 10³ L at room temperature.
bombarded surface (i.e., Ti$^{+3}$-free surface) induce three other distinct photoelectron emissions at -13.4, -10.9, -7.1 eV, and a very small emission at -4.5 eV. The work function is found to decrease by -0.5 eV. This is in striking contrast to the water adsorption on the room temperature Ar ion bombarded SrTiO$_3$ surface which causes an increase in the work function of +0.5 eV.

The chemisorption of hydrogen on the Ar ion bombarded surfaces at 27°C and 600°C are shown in Figs. 7.6 and 7.7 respectively. We notice on the room temperature Ar ion bombarded surface there are three chemisorbed hydrogen-induced emissions at energies of -10.6, -6.2, and -4.7 eV and a work function increase of +0.2 eV while on the high temperature (600°C) Ar ion bombarded surface adsorption of hydrogen induces four emissions at energies of -13.4, -11.0, -6.9, and -4.3 eV, and a work function decrease of -0.2 eV.

Recent studies of clean SrTiO$_3$ surface$^{(3)}$ reveal that the pretreatment of the surface plays a very important role in determining the surface chemical composition and the associated surface electronic distribution. Ar ion bombardment at 27°C gives a Ti$^{+3}$-rich surface of Auger ratios Sr/O = 2.8 and O/Ti = 2.2, while Ar ion bombardment at 600°C gives a Ti$^{+3}$-free surface of Auger ratios Sr/O = 4.1 and O/Ti = 2.2. Since the application of UPS spectroscopy in chemisorption can give the valence electron distribution of the adsorbed molecules, the marked differences shown in the UPS spectra for chemisorption of H$_2$O and H$_2$ on the SrTiO$_3$ surfaces after different treatments indicate the nature of the adsorbed surface complex must be very different from each other and depend strongly on the chemical composition and Ti$^{+3}$ concentration of the substrate surface.
Fig. 7.6. UPS N(E) spectra of the Ar ion sputtered (at 27 C) SrTiO₃ surface before and after a H₂ exposure of 9 x 10³ L at room temperature.
Fig. 7.7. UPS N(E) spectra of the Ar ion sputtered (at 600 C) SrTiO$_3$ surface before and after a H$_2$ exposure of 9 x 10$^3$ L at room temperature.
Figure 7.8 shows the UPS difference spectra, $\Delta N(E)$, for water adsorption on SrTiO$_3$(111)-(1x1) and a room temperature Ar ion bombarded surface. Both surfaces have significant Ti$^{+3}$ concentration. The two spectra are quite similar to chemisorbed H$_2$O spectrum on the reduced TiO$_2$ surface but they are quite different from that of undissociated water.$^{(2)}$ Recent calculation by Tsukada et al.$^{(4)}$ indicates that OH$^-$ may be formed on the reduced TiO$_2$ surface. From our result it appears that the water adsorbs dissociatively on surfaces of TiO$_2$ and SrTiO$_3$ which have significant Ti$^{+3}$ concentration. This is further supported by the observation that the chemisorbed H$_2$ and H$_2$O on the room temperature Ar ion bombarded SrTiO$_3$ surface have very similar photoemission spectra (in Fig. 7.8). If we assume that the hydrogen molecule dissociates on adsorbing to the surface by interacting with surface Ti$^{+3}$ species, then due to the presence of oxygen in the strontium titanate oxide lattice, the dissociated hydrogen atom will tend to react with oxygen ions to form surface hydroxyl groups.

The photoemission difference spectra, $\Delta N(E)$, for chemisorbed water and hydrogen on the high temperature (600°C) Ar ion bombarded SrTiO$_3$ surface are shown in Fig. 7.9. Recent study$^{(2)}$ of clean SrTiO$_3$ surface indicates Ar ion bombardment at 600°C results in a Sr-rich oxide surface with no Ti$^{+3}$ present. This change in the surface composition of the substrate seems to be the reason for the differences between Fig. 7.8 and Fig. 7.9. The nature of the adsorbed species shown in Fig. 7.9 is not known; but the close resemblance of the UPS spectra between chemisorbed hydrogen and water suggests that either adsorbed water dissociates to form hydrogen or adsorbed hydrogen reacts with surface oxygen to form H$_2$O.
Fig. 7.8. UPS $\Delta N(E)$ spectra for (a) $\text{H}_2\text{O}$ adsorbed on $\text{SrTiO}_3$\((1\text{I})-(1\times1)\) surface; (b) $\text{H}_2\text{O}$ adsorbed on Ar ion bombarded (at 27 C) $\text{SrTiO}_3$ surface; and (c) $\text{H}_2$ adsorbed on Ar ion bombarded (at 27 C) $\text{SrTiO}_3$ surface.
Fig. 7.9. UPS $\Delta N(E)$ spectra for (a) H$_2$O, and (b) H$_2$ adsorbed on Ar ion bombarded (at 600 C) SrTiO$_3$ surface.
Further thermal desorption experiments will provide more insight in elucidating the nature of the adsorbed species.

7.4. Chemisorption of CO, CO₂ on the SrTiO₃ Surfaces in the Dark and in the Light

Both CO and CO₂ give rise to the same UPS N(E) spectra as shown in Fig. 7.10 when adsorbed on the SrTiO₃ surface. The measurements were taken after exposure of the surface to 5 x 10⁴ L of these gases. The work function is found to increase by 0.4 eV and 0.5 eV on adsorption of CO₂ and CO respectively. The Ti⁺³ signal is significantly decreased. On illumination there is no noticeable change in either the work function or the Ti⁺³ signal. Upon heating the sample after CO adsorption, only CO₂ is observed to desorb, indicating that CO may be efficiently converted to CO₂ on the SrTiO₃ surface.

There is considerable experimental evidence indicating that CO is readily oxidized to CO₂ over several transition metal oxide surfaces in addition to SrTiO₃. An oxygen ion from the crystal lattice is likely to be used for this purpose. This fact is supported by the AES spectra shown in Fig. 7.11 where after flashing the CO-covered surface, change in the shapes of Auger Ti (412 ev) and Ti (419 ev) transitions indicates the surface has been reduced by the reaction: CO + O(surface) → CO₂(desorbed). The reduction of CO₂ to CO that is commonly observed on many transition metal surfaces does not appear to occur on the oxide surface. Another reaction that converts CO to CO₂ on the oxide surface is its proportionation: 2CO → C + CO₂. We cannot rule out this reaction as a possible path in converting CO to CO₂ on the SrTiO₃ surface, although we do not see the accumulation of much carbon on the surface after flashing.
Fig. 7.10. UPS $\Delta N(E)$ spectra for CO$_2$ and CO adsorbed on SrTiO$_3$(111)-(1x1) surface.
Fig. 7.11. AES spectra for (a) clean SrTiO$_3$ (111)-(1×1) surface; (b) CO adsorbed on SrTiO$_3$ surface; and (c) after flashing CO covered SrTiO$_3$ surface. Note the change in the ratio of Ti(412 eV)/Ti(419 eV) Auger peaks.
the CO-covered surface.

7.5. **Coadsorption of CO$_2$ and H$_2$O on the SrTiO$_3$ Surface**

We have coadsorbed H$_2$O and CO$_2$ on the SrTiO$_3$(111)-(1×1) surface in the dark and in the light. The experimental procedures were taken as follows: we first prepared a clean ordered SrTiO$_3$(111)-(1×1) surface and exposed this surface to $10^4$ L CO$_2$; then this partially CO$_2$-covered surface is exposed to $10^4$ L H$_2$O. After the adsorption of CO$_2$ and H$_2$O, the gas covered surface is exposed to UV light for $10^3$ seconds. The UPS spectra for the sequence of gas adsorptions and light illumination are shown in Fig. 7.12. We also reversed the sequence of coadsorption of CO$_2$ and H$_2$O and obtained similar photoemission spectra. We see that after UV light illumination, there is an increase in photoelectron emission of energies between -8 eV and -4 eV. This may be due to the photo-induced reaction between CO$_2$ and H$_2$O at the surface. Further studies using other complementary techniques like I.R. and XPS are needed to elucidate the nature of the surface complex after CO$_2$ and H$_2$O coadsorption in the dark and in the light.

7.6. **Conclusion**

In this chapter we have shown conclusively that the nature of the adsorbed surface complexes depend strongly on the chemical composition and the associated electronic distributions of the strontium titanate substrate surface. Since the main function of a solid surface in heterogeneous catalysis is to form intermediate surface complex with the reactant molecules (thereby offering an alternative reaction path which
Fig. 7.12. UPS N(E) spectra for coadsorption of H$_2$O and CO$_2$ on the SrTiO$_3$(111)-(1x1) surface, before and after light illumination.
allows a higher reaction rate for a specific reaction) our results indicate the possibility of performing chemical reactions with unique selectivity and high reaction probability by appropriate choice of the catalytic active surface. The roles of surface Ti$^{+3}$ and light are clearly demonstrated. Surface Ti$^{+3}$ species decompose water into surface hydroxyl groups. The adsorbed oxygen and water oxidize surface Ti$^{+3}$ to Ti$^{+4}$. In order to sustain the decomposition of water into hydrogen and oxygen, light is needed to replenish these Ti$^{+3}$ species.

From chemisorption studies, there is evidence for the oxidation of CO to CO$_2$ at the SrTiO$_3$ surface. Thus we attempt to rule out the conversion scheme of CO$_2$ to CO and then into dissociated oxygen and carbon on the SrTiO$_3$ surface. A more likely path leading to photo-assisted formation of CH$_4$ may be the hydrogenation of CO$_2$ with water to form formic acid (HCOOH) or formaldehyde (H$_2$CO) with further reduction to CH$_4$. Further studies will be needed toward verifying the reaction intermediates.

It is likely that other molecules, in addition to methane, may also be produced using other appropriate substrate surface, light of suitable wavelength, and gas mixtures of CO$_2$, H$_2$O and N$_2$. Indeed, light assisted reactions over semiconductor surfaces may provide new routes for the production of many different small molecules, which are thermodynamically forbidden in the dark.
Chapter 7: References

APPENDIX 1: ULTRAVIOLET PHOTOEMISSION STUDIES OF ACETYLENE AND ETHYLENE ADSORPTION ON THE Pt(111) SURFACE AS A FUNCTION OF TEMPERATURE: CORRELATIONS WITH LEED STUDIES

The chemisorption of acetylene (C₂H₂) on the Pt(111) single crystal surface has been studied using low-energy electron diffraction (LEED) by several authors. (1-4) It has been well established under conditions of low acetylene exposure (3 Langmuirs) to the clean metal surface in ultrahigh vacuum that the adsorbed acetylene forms a well ordered overlayer structure with a diffraction pattern characteristic of a (2×2) unit mesh. By measuring the diffraction beam intensities from this system as a function of electron energy, Stair and Somorjai (3) found that adsorption took place in two steps: first, acetylene adsorbed at 300°K into a metastable state followed by the chemical conversion into another more stable state upon heating to 350°K. Both structures showed the characteristic (2×2) diffraction patterns which could be distinguished only through changes in the diffraction beam intensity profiles (I vs. eV curves). By adsorbing ethylene (C₂H₄) on the same Pt(111) crystal at 300°K followed by low-energy (100 eV) electron beam exposure, they found that the initially disordered adsorbate yielded the same (2×2) diffraction pattern with the I vs. eV curves identical to those of the more stable acetylene structure. 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. (4) have shown that the bonding of the molecule in the more stable acetylene state occurs at a triangular site 1.95 Å above the plane of Pt atoms,
the carbon atoms coordinating at covalent bonding distances to three surface platinum atoms. Analysis of the metastable acetylene structure is at present complete, and preliminary evidence indicates the molecule is farther away from the surface in this state and hence less strongly bound.

In the past few years ultraviolet photoelectron spectroscopy (UPS) has been quite successfully used to study the chemisorption state of adsorbed molecules on the transition metal surfaces.\(^5\) It is of importance to apply UPS in investigating 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 Pt(111) surface employing experimental conditions that are identical to those utilized in the LEED studies.\(^3\) 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 Pt(111) surface as well.

All the experiments were performed in an ultrahigh vacuum chamber (\(P \sim 1 \times 10^{-10}\) torr) equipped with HeI (\(h\nu = 21.2\) eV) discharge lamp, double pass cylindrical mirror analyzer (CMA) with internal coaxial gun, LEED optics and quadrupole mass spectrometer. The Pt(111) single crystal surfaces were cleaned by argon ion sputtering and heating (1000 K) in an oxygen atmosphere. Surface characterization was performed by LEED, Auger electron spectroscopy (AES), and UPS. The energy of the photoemitted electron was analyzed with a double-pass (angle-integrating) cylindrical
analyzer operated in a constant retarding mode so as to have a resolution of 0.15 eV. The angle of incidence of the photons on the sample was 75° from the axis of CMA. Two orientations of the sample have been used with the sample in a normal direction, either 75° or 67.5° from the incident photon beam. The same results were obtained independently of these two orientations. In order to remove the acetone (CH₃COCH₃) that is 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. 1a we show the photoemission difference spectrum, ΔN(E), for Pt(111) after exposure to 3L (1L = 1×10⁻⁶ torr/second) acetylene for hv = 21.2 eV with a sample temperature of 300 K. The energy scale 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, a distinct (2×2) pattern could be seen by LEED. After heating this chemisorbed C₂H₂ surface structure to 350°K for one hour 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 ΔN(E) in Fig. 1b. 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
Fig. A1.1. Photoemission difference curves $\Delta N(E)$ relative to $E_F$ for (a) metastable acetylene state after 3L acetylene exposure on the Pt(111) surface at room temperature (300K). Preliminary identification with the molecular orbitals of gas phase acetylene is indicated; (b) the stable acetylene state after heating the adsorbed acetylene on the Pt(111) surface to 350K for an hour.
eV to -4.0 eV. The ratio of these two emission intensities was about 3 to 1 as seen in Fig. 1b. The LEED pattern showed the same (2×2) ordered overlayer structure except that the spot intensities changed, consistent with the findings of the previous LEED analysis.(3) After saturating the Pt(111) surface with 103 L acetylene exposure, the UPS spectra remained unchanged. However, the long range (2×2) ordering was destroyed and the work function change was higher (-1.0 eV) for this saturated condition.

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

We find there is a very close correlation between the changes in the UPS spectra and the structural transitions detectable by LEED from chemisorbed acetylene on the Pt(111) surface. Both techniques reveal that chemisorbed acetylene on Pt(111) surfaces at room temperature (300°K) is in a metastable state. It can be converted into a more stable state by a gentle heating for an hour, and this transformation is observed by marked changes in the UPS spectra. In addition, we find that at room temperature ethylene dehydrogenates to acetylene which is still in a disordered state on the Pt(111) surface. The incident electron beam
Fig. A1.2. Photoemission difference curve $\Delta N(E)$ for chemisorption of ethylene on the Pt(111) surface at room temperature.
merely orders the already dehydrogenated species. This information could not be obtained by LEED analysis alone since LEED studies are insensitive to the properties of disordered adsorbates.

By comparison with the gas phase spectrum of acetylene molecules (6) we can associate the \( \text{C}_2\text{H}_2 \) induced emission at \(-3.8\) eV and \(-8.2\) eV (Fig. 1a) to the acetylene \( 1\pi_u \) and \( 3\sigma_g \) molecular orbitals. Assuming uniform relaxation shifts, (5) there is a 0.6 eV chemical bond shift for \( \pi \)-orbitals due to the bonding between acetylene \( \pi \)-orbitals and Pt atoms on the surface of 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 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 lower state which is associated with the \( 3\sigma_g \) orbital shifts from \(-8.2\) eV to \(-7.8\) eV. This may arise from either an increased relaxation effect due to decreasing distance from the surface (5) or the increase of carbon-carbon distance within the acetylene molecule. (7) The nature and degree of the indicated rehybridization in terms of surface-induced CC bond elongation and CCH angle bending cannot be ascertained from the limited data available to us with the 21.2 eV HeI 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 Pd(111) by Demuth. (8)

Dynamical LEED analysis of the metastable \( \text{C}_2\text{H}_2 \) state on Pt(111) surfaces has been performed by Kesmodel et al, (4) whose result shows
the metastable $\text{C}_2\text{H}_2$ to be coordinated to basically one surface Pt atom at a distance of 2.45 Å. Recently Baetzold\cite{9} completed theoretical calculation of valence electron energy distribution of the stable species formed from $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ chemisorption on the Pt(111) surface, assuming various surface hydrocarbon species with different chemical structures. The comparison of the theoretical calculation with the experimental photoelectron emissions, as shown in Fig. 3, reveals that the stable species on the Pt(111) surface after $\text{C}_2\text{H}_2$ or $\text{C}_2\text{H}_4$ chemisorption is ethylidyne, $\text{C-CH}_3$. This result is consistent with those of LEED structural analysis\cite{10} and high resolution ELS analysis\cite{11}.

In summary, combination of UPS, LEED structural analysis, and high resolution ELS results indicates the overall reaction of $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ on the Pt(111) may be written as follows:

$$
\begin{align*}
\text{C}_2\text{H}_2(\text{g}) & \rightarrow \text{metastable}(\text{C}_2\text{H}_2)^* \\
300 \text{ K} & \\
\text{H}^* & \rightarrow (\text{+C-CH}_3)^* \\
350 \text{ K} & \\
\text{C}_2\text{H}_4(\text{g}) & \rightarrow (\text{+C-CH}_3)^* + \text{H}^* \\
300 \text{ K} & 
\end{align*}
$$

where (*) indicates a surface species. The extra hydrogen necessary for the acetylene reaction comes from background hydrogen in the ultra-high vacuum chamber.
Stable species formed from \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) chemisorption on Pt(III).

Fig. A1.3. The comparison of experimental photoemission spectrum of Fig. A1.2 with the theoretical calculation of valence orbitals of different surface complexes.
APPENDIX 1: REFERENCES

9. R.C.Baetzold, unpublished result.
10. L.L.Kesmodel, L.H.Dubois, and G.A.Somorjai, to be published.
APPENDIX 2. LOW ENERGY ELECTRON DIFFRACTION AND ELECTRON SPECTROSCOPY STUDIES OF THE CLEAN (110) AND (100) TITANIUM DIOXIDE (RUTILE) CRYSTAL SURFACES

ABSTRACT

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss (ELS) and ultraviolet photoemission spectroscopies (UPS) were used to study the structures, compositions, and electron state distributions of clean single crystal faces of titanium dioxide (rutile). LEED showed that both the (110) and (100) surfaces are stable, the latter giving rise to three distinct surface structures, viz. (1x3), (1x5), and (1x7) that were obtained by annealing an argon ion-bombarded (100) surface at ~600, 800, and 1200°C respectively. AES showed the decrease of the O(510eV)/Ti(380eV) peak ratio from ~1.7 to ~1.3 in going from the (1x3) to the (1x7) surface structure. Electron energy loss spectra obtained from the (110) and (100)-(1x3) surfaces are similar with surface-sensitive transitions at 8.2, 5.2, and 2.4 eV. The energy loss spectrum from an argon or oxygen ion bombarded surface is dominated by the transition at 1.6 eV. UPS indicated that the initial state for this ELS transition is peaked at -0.6 eV (referred to as the Fermi level E_F) in the photoemission spectrum, and that the 2.4 eV surface-sensitive ELS transition probably arises from the band of occupied states between the bulk valence band maximum to the Fermi level. High energy electron beams (1.6 keV 20 μA) used in AES were found to disorder clean and initially well-ordered TiO_2 surfaces. Argon ion bombardment of clean ordered TiO_2(110) and (100)-(1x3) surfaces caused the work function and surface band bending to decrease by almost 1 eV and such a decrease is explained as due to the loss of oxygen from the surface.
1. INTRODUCTION

Recently, several interesting studies were reported on the photoassisted and photocatalytic reactions of gases on titanium dioxide powders.\(^{(1-4)}\) It is established by these studies that light with energy greater than about 3 eV (band gap energy of TiO\(_2\)) plays an important role in such reactions. However, the detailed reaction mechanism is not understood, mostly for two reasons. First, most studies were carried out on TiO\(_2\) powders so that essentially all crystal faces were exposed. There is ample evidence from single crystal surface studies\(^{(5)}\) that chemisorption characteristics change markedly from crystal surface 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 TiO\(_2\) 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 of each individual crystal face.

Another motivation for our TiO\(_2\) 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.\(^{(6-8)}\) However, such a photoelectrolysis process can only be sustained by applying a positive potential, \(\sim 0.5\) V, to the titanium dioxide electrode. Without an applied potential the surface
band-bending on the TiO$_2$ electrode is too small to allow an efficient separation of the photogenerated electron—hole pairs$^{(8)}$ which appears to be a necessary step in the photoelectrolysis process. An increase in the band-bending of $\geq 0.5$ V on the TiO$_2$ surface without an externally applied potential is desirable in practical applications as solar energy conversion devices. This necessitates a detailed study and understanding on how the surface band-bending can be varied by changing the surface conditions.

Except for the work of Henrich et al.$^{(9)}$ 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 paper we report on studies of clean titanium dioxide (rutile) single crystal surfaces of (110), (100), and (001) orientations. Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to characterize surface structures and compositions respectively. Electron states distributions were studied by electron energy loss spectroscopy (ELS) and ultraviolet photoemission spectroscopy (UPS). Information on the work function and surface band-bending was obtained from the photoelectron distribution curves.

2. EXPERIMENTAL TECHNIQUES

All experiments were performed inside an ion-pumped stainless steel vacuum system with a base pressure of less than $1 \times 10^{-10}$ torr. The system was equipped with LEED optics, ion bombardment gun, a quadrupole mass spectrometer and a helium resonance lamp. A double-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun was used as the primary
electron source and electron energy analyzer. In all AES analyses, the CMA was operated at a constant resolution of 1.5 eV. In this way, we could resolve detailed structures of the peaks in Auger spectra and give reliable estimates of the oxygen-to-titanium ratios under different conditions of surface preparation.

In obtaining the electron energy loss spectra, the analyzer was operated in the retard mode with pass energy set at 50 eV. However, since the primary electron beam was not energy analyzed, the ultimate resolution was limited by the thermal energy spread of the incident electrons, which was about 0.5 eV. The features in the loss spectrum were enhanced by measuring the second derivative \(-d^2N/dE^2\) of the electron energy distribution as a function of energy loss. The energy positions of the loss peaks were independent of incident electron energies in the range of 50 to 200 eV. All loss spectra reported in this paper were obtained with incident energies \(\sim 100\) eV, which represents a compromise between good surface sensitivity and large signal-to-noise ratio.

In UPS studies, the resonance lamp was operated to generate the HeI spectral line at 21.2 eV. A two-stage differential pumping manifold was employed to minimize the helium leak flow from the discharge lamp into the ultra-high vacuum chamber, which maintained a pressure of \(1-2 \times 10^{-9}\) torr during all UPS experiments. The specimen was positioned with its surface normal coincidence with the axis of the CMA. The angle of incidence of the photons on the specimen was 75° from the normal. The emitted photoelectrons were collected at \(\theta = 42^\circ\) over all azimuth angles by the CMA. The analyzer was operated with a constant resolution of 0.35 eV. Typically a spectrum could be obtained in 5 to 10 min.
The specimen used was a 99.99% 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 μm 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.

For argon (resp. oxygen) ion bombardment of titanium dioxide surfaces, the vacuum chamber was back-filled with argon (resp. oxygen) to a pressure of 6 × 10⁻⁵ torr (resp. 1 × 10⁻⁵ torr). With an accelerating voltage of 2 kV, the ion bombardment gun could typically deliver an argon (resp. oxygen) ion beam of 8 μA (resp. 1 μA) to the sample surface.

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 Å and c = 2.96 Å (Fig. 1). Physical properties such as electrical conductivity and dielectric constant are highly anisotropic.

TiO₂ is a partially ionic semiconductor. One can consider the valence and conduction bands to be derived mainly from the O(2p) and Ti(3d) orbitals respectively. The optical band gap is 3.0 eV near room temperature. The pure undoped crystal is thus transparent with a yellowish tint.

The phase diagram of the O-Ti system is complicated. Below
Fig. A2.1. The titanium dioxide (rutile) crystal lattice.
~1830°C (m.p. of TiO₂), there exist at least eight intermediate titanium oxides (TiₙO₂₋ₙ₋₁, n=3 to 10) between Ti₂O₃ and TiO₂. On reduction by heating in vacuum or hydrogen at 600°C for an hour, oxygen is partially lost from the TiO₂ lattice (equilibrium oxygen partial pressure above TiO₂ at 600°C being about 10⁻¹⁸ torr) 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 Ti³⁺ species. The oxygen concentration can be restored by heating the reduced crystal in an oxygen atmosphere (~200 torr) at 600°C for 1 hr, as shown by the color change of the crystal from blue to yellow.

4. RESULTS

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°C removed carbon, but resulted in the segregation of potassium and calcium. In order to produce a clean surface the crystal must be heated to a temperature of 800-900°C during argon ion sputtering for ~10³ sec before annealing. The Auger electron spectra for clean argon ion-bombarded and annealed (at 600°C) TiO₂(110) surfaces are shown in Fig. 2. Note the increase in the O(510eV)/Ti(380eV) ratio from ~1.3 on the argon ion bombarded surface to ~1.7 on the annealed TiO₂(110) surface. This ratio is fairly reproducible over many sputtering-
Fig. A2.2. Auger electron spectra of (a) argon ion bombarded and (b) annealed TiO$_2$ (110) surface.
annealing cycles on different crystal faces of TiO₂. On the other hand, on bombarding a clean and well ordered TiO₂(110) surface at room temperature with ~7.2 × 10¹⁵ oxygen ions/cm², the O(510)/Ti(380) ratio remains essentially unchanged, viz.-1.7.

LEED showed that the (110) surface has a stable (1×1) unreconstructed structure after annealing at 600-800°C (Fig. 3). On the other hand, three distinct clean surface structures were found on the (100) surface by annealing an argon sputtered (100) surface at different temperatures (Fig. 4). Annealing at 500-600°C resulted in a (1×3) surface structure. Further annealing up to 800°C gave rise to a (1×5) structure. A surface with a (1×7) structure was obtained when a crystal was heated at ~1200°C for a few seconds. All these structures are stable at room temperatures, and can be generated by annealing a freshly argon sputtered surface at temperatures indicated above.

While the Auger electron spectra for these different surface structures on the (100) surface are all similar to that shown in Fig. 2b, there is a large variation in the O(510eV)/Ti(380eV) ratio, decreasing from ~1.7 for the (1×3) surface to ~1.3 for the (1×7) 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). 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
Fig. A2.3. LEED pattern from a clean ordered TiO$_2$(110) surface at an electron incident energy of 92 eV.
TiO$_2$(100)

(1 x 3)  (1 x 5)  (1 x 7)

Fig. A2.4. LEED patterns from clean TiO$_2$(100)-(1×3), (1×5), and (1×7) surfaces. The primary electron energies are 110, 62 and 60 eV respectively.
Fig. A2.5. 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.
in the LEED pattern or the Auger spectrum. However, a 2-min exposure to a 1.6 kV, 20 A electron beam (typically of AES operation) resulted in observable blurring of the LEED spot pattern, while the O/Ti ratio on the surface was unaffected by such irradiations.

When a clean well-ordered TiO$_2$ (110) or (100)-(1×3) surface was exposed briefly (30 min to an hour) to the ambient atmosphere, the LEED spot pattern was preserved, with some increase in the background intensity. AES indicated only a small (~0.1 monolayer) contamination on the crystal surface. For an argon sputtered TiO$_2$ surface exposed to the same ambient under similar conditions, the carbon contamination was ≥0.5 monolayer.

4.2. Electron Energy Loss Spectroscopy

On the argon or oxygen ion bombarded TiO$_2$ (100) surface the energy loss spectrum (Fig. 6a) 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 (1×3) surface structure, 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 peak and the complete disappearance of the 1.6 eV transition (Fig. 6b). The (110) surface gives rise to a loss spectrum similar to that of the (100)-(1×3) surface. On the (100)-(1×5) surface, the energy loss spectrum shows the reappearance of the 1.6 eV transition (Fig. 6c). The (1×7) surface has a loss spectrum similar to that of the (1×5) 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 (1×3) surface, transitions at 8.2, 5.2 and 2.4 eV are all surface sensitive, whereas
Fig. A2.6. Electron energy loss spectra of (a) argon ion bombarded TiO$_2$(100), (b) TiO$_2$(100)-(1×3), and (c) TiO$_2$(100)-(1×5) surfaces. Transitions labeled with (*) are surface-sensitive.
transitions at 13.5, 10.1, and 5.8 eV are due to bulk TiO₂ interband excitations.⁹

High energy electron beams were found to have a significant effect on the energy loss spectra of TiO₂ surfaces. Figure 7 shows the energy loss spectra from a freshly annealed (110) surface and the same surface irradiated by a 1600 eV 20 µA electron beam for 100 sec. The latter spectrum closely resembles that from an argon ion sputtered surface.

4.3. Ultraviolet Photoemission Spectroscopy

The UPS spectra for different TiO₂ surfaces are shown in Fig. 8. In agreement with the work of Henrich et al.,⁹ we found a band gap emission at 0.6 eV below the Fermi level E_F on the argon ion bombarded TiO₂(110) surface (Fig. 8a). In addition, a peak at -10.6 eV (referred to the Fermi level) was found. The same two UPS emissions were also observed on the oxygen ion bombarded TiO₂(110) surface (Fig. 9). Annealing at 600°C resulted in the weakening of these two peaks, altogether with marked changes in the valence band emission, as shown in Fig. 8b.

The valence band structure of the TiO₂(100)-(1x3) surface is distinctly different from that of the ordered (110) surface. Note the characteristic step structure in the valence band emission at -5.3, -6.4, and -8.0 eV (Fig. 8c). The UPS spectrum of the (100)-(1x5) closely resembles that of the (1x3) surface, except for the increase of the peak at -5.3 eV relative to the emission at -6.4 and -8.0 eV (Fig. 8d). 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 (=hν: the width of photoelectron energy distribution) increased from 4.6 eV for the TiO₂(110) argon
Fig. A2.7. Effect of electron beam irradiation on the TiO₂(110) surface. The dotted curve is the loss spectrum from a freshly annealed TiO₂(110) surface and the solid curve is the spectrum from the same surface after being irradiated by 1.6 kV 20 μA electron beams for 100 seconds.
Fig. A2.8. UPS spectra for various TiO$_2$ surfaces, obtained with $h\nu = 21.2$ eV at a resolution of 0.35 eV. The secondary background has been subtracted and all energies are referred to the Fermi level:

(a) argon ion bombarded (110) surface; (b) ordered (110) surface; (c) (100)-(1x3) surface, and (d) (100)-(1x5) surface.
Fig. A2.9. UV photoemission spectrum from an initially clean and well-ordered TiO$_2$(110) surface irradiated by $7.2 \times 10^{15}$ ions/cm$^2$, obtained with $h\nu = 21.2$ eV at a resolution of 0.35 eV.
bombarded surface to 5.5 eV for the well annealed (110) surface. This result is consistent with that of Henrich et al (9) reported for the (110) surface. On the other hand, the work function of an initially well ordered TiO$_2$(110) surface was unaffected by oxygen ion bombardment up to $7.2 \times 10^{15}$ ions/cm$^2$. From the photoelectron energy distribution, one can further estimate the energy position (referred to the Fermi level) of the bulk valence band maximum 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 (14) a surface band-bending of $1.7 \pm 0.2$ eV for both the annealed or oxygen ion-bombarded (110) and (100)-(1×3) surface and $0.9 \pm 0.2$ eV for the argon ion bombarded surface.

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 both (110) and (100) surfaces. 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 the oxygen from the bulk to the surface and the escape of oxygen from the surface. After using the crystal for many sputtering-annealing cycles, the O(510eV)/Ti(380eV) ratio on the surface drops to below the normal value of ~1.7 on the
(100)-(1×3) and (110) surfaces annealed at 600°C. When this occurs, the crystal must be re-oxidized to establish the original O/Ti ratio.

While AES shows oxygen loss from the TiO₂ surface as a result of argon sputtering, the energy loss spectrum of the argon ion sputtered TiO₂ surface shows a strong transition at 1.6 eV. In agreement with the interpretation of Henrich et al.⁹ this indicates that this peak is due to a Ti³⁺ interband transition. The same 1.6 eV ELS transition was also found on TiO₂ surfaces disordered by oxygen ion or high energy electron beam bombardment, in which the surface oxygen concentration remained unchanged, as well as in the TiO₂(100)-(1×5) and (1×7) surfaces, in which a decrease of the surface oxygen concentration occurred. Therefore, it appears that surface Ti³⁺ species are formed as a result of either the displacement oxygen from normal lattice sites (no change in the O/Ti ratio) or loss of oxygen from the crystal surface (decrease in the O/Ti ratio).

The appearance of the 1.6 eV ELS transition in the energy loss spectrum of the TiO₂ surface bombarded with ions (argon or oxygen) 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, in agreement with reference (9). Since the band gap of TiO₂ is 3 eV, the initial state for the ELS transition at 2.4 eV on ordered TiO₂ surfaces must be located slightly above the bulk valence band maximum. Indeed, a non-zero density of occupied states extending from the bulk VBM to the Fermi level was found on all TiO₂ surfaces (Fig. 8).
On the argon (oxygen resp.) ion bombarded surface, a UPS peak at -10.6 eV (-10.3 eV resp.) 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 of both the annealed (110) and (100) surfaces indicates that this is probably due to the anisotropy of photoelectron emission from this state. By detecting the photoelectrons emitted in all directions with a spherical collector, Derbenwick(15) 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.

There have been several studies made on the room temperature adsorption of oxygen on freshly evaporated titanium films.(16,17) The UPS spectra so obtained compare very closely with those from TiO$_2$ surfaces disordered by oxygen ion bombardment. For example, in Eastman's work,(17) exposing the titanium film to 100L (1L = 10$^{-6}$ torr-sec) of oxygen at room temperature gives rise to two UPS peaks at -4.9 and -6.7 eV and a residual titanium d band emission near the Fermi level. The peak positions of the oxygen induced emission are almost identical to those
obtained for the oxygen ion-bombarded TiO$_2$ surfaces in our work (Fig. 9). This confirms Eastman's suggestion (17) that a (disordered) TiO$_2$ layer is formed on the surface as a result of oxygen adsorption on the titanium film surface.

It is interesting to find that different surface treatments of the TiO$_2$ surface result 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, while oxygen ion bombardment up to $7.2 \times 10^{15}$ ions/cm$^2$ causes no observable changes. 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. One electron is trapped by a neighboring Ti$^{4+}$ to give Ti$^{3+}$ (which shows up in the UPS spectrum as an emission peaked at -0.6 eV), whereas the other electron is essentially free. This increases the surface free electron concentration (18,19) thereby causing a decrease in the surface band-bending. Clearly, these changes have profound effects (20) 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 carrier at the surface (e.g., transport of holes to the TiO$_2$ surface during photoelectrolysis) is the rate-determining step, (8) it is desirable
to increase the surface band-bending to allow a rapid charge transport
to and away from 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 in this work,
may be of importance in controlling photo-induced surface reactions.

6. CONCLUSION

In this study we demonstrated the ability of LEED and various
electron spectroscopy techniques in studying and characterizing 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. (1×3), (1×5) and (1×7) 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.

In agreement with Henrich et al., (9) argon ion bombardment was found
to remove oxygen preferentially from the TiO$_2$ 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)-(1×3), (1×5),
and (1×7) surface structures correlates with the decrease in the
O(510eV)/Ti(380eV) ratio from ~1.7 to ~1.3, as shown by AES.

The (110) and (100)-(1×3) 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)-(1×5) and (1×7) surfaces.
On the argon or oxygen ion bombarded surface, a well-defined ELS transition at 1.6 eV was found, which is believed to arise from surface Ti$^{3+}$ species\(^{(9)}\) due to the displacement of oxygen from normal lattice sites or loss of oxygen from the surface. UPS spectra from these surfaces indicate that the band gap emission at -0.6 eV from $E_F$ can be attributed to be the initial state for the 1.6 eV ELS transition on argon or oxygen ion bombarded TiO$_2$ surface. The band of occupied states extending from the bulk valence band maximum to the Fermi level is likely to be the initial state for the 2.4 eV ELS transition on all ordered surfaces. Comparison of the photoelectron energy distribution from the oxygen ion bombarded TiO$_2$ surface with recent work on oxygen adsorption on titanium film surface\(^{(16,17)}\) suggests that a disordered TiO$_2$ layer is formed by exposing a freshly evaporated titanium film to ~100 L oxygen at room temperature.

Low energy (50 to 200 eV) electron irradiation does not have any observable effects on the surface composition, structure, and electron state distribution of clean TiO$_2$ surfaces. However, initially clean and well ordered TiO$_2$ surfaces are disordered by electron beams normally used in Auger analysis (1.6 kV, 20 μA), as demonstrated by LEED, energy loss and ultraviolet photoemission spectroscopies from these surfaces. The work function and band-bending of clean ordered TiO$_2$ (110) and (100)-(1X3) 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, 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 and we are currently pursuing chemisorption studies of H₂, O₂, and H₂O on different single crystal faces of titanium dioxide with this objective.
APPENDIX 2: REFERENCES

14. 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 minus 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, the possible variation of electron
affinity as a result of surface oxygen concentration is not included. We believe that such variation is small in comparison with band bending changes because the electron affinities for both Ti and TiO$_2$ are $\sim$4 eV and we do not expect a significant deviation from the trend of variation of electron affinity as a function of the oxygen concentration for intermediate compositions.


APPENDIX 3. PHOTOASSISTED REACTIONS BY THE Pt-SrTiO$_3$ SINGLE CRYSTAL SANDWICH. THE ADSORPTION OF GASEOUS H$_2$O AND CO$_2$ AND THE PRODUCTION OF CH$_4$ AT THE SOLID-GAS INTERFACE.

ABSTRACT

We report on the photochemical production of CH$_4$ from gaseous CO$_2$ and H$_2$O in contact with a sample consisting of a SrTiO$_3$(111) single crystal in contact with Pt foil. Radiation with energy greater than the SrTiO$_3$ band gap is effective in photoassisting the reaction. The reaction was studied at total gas pressures of ~30 torr and 300°K and as a function of temperature.

Ultraviolet photoemission spectroscopy and electron energy loss spectroscopy have been used to study the chemisorption of H$_2$O, CO$_2$, O$_2$ and CO on SrTiO$_3$ single crystals. The results of these studies shed light on the mechanism of the methane production photoreaction.

1. INTRODUCTION

There are only a few widely utilized catalytic reactions that are thermodynamically "uphill," i.e., accompanied by a large positive free energy change, but they are of great importance. One is photosynthesis which produces hydrocarbons and oxygen from carbon dioxide and water, and light provides the external energy source necessary for its completion. The other, the electrolytic dissociation of water to hydrogen and oxygen, utilizes an external potential as a source of energy to carry out the electrode reactions. Recently, there have been successful attempts to dissociate water in an electrochemical cell by using light instead of an external potential.$^{(1-5)}$ Oxygen evolves at the oxide (SrTiO$_3$, TiO$_2$)
anode and hydrogen at the cathode (Pt or p-type GaP) from a basic aqueous electrolyte solution when light of band gap energy (about 3 eV) illuminates the anode. This photoassisted reaction seems to take place even if the anode and cathode are short circuited, i.e., touching each other. (1)

We have embarked on a program to explore the possibility of producing small hydrocarbon molecules from CO₂ and H₂O, at the solid vapor interface, with the assistance of light. Light, as an energy source, may be utilized to create electron hole-pairs by direct excitation across the band gap of an insulator or semiconductor, or it may be used for direct excitation of the reactant molecules. We convert light to electron-hole pairs in the excited solid similar to the way it is utilized in the photographic process. The charge carriers must then be trapped by the reactants before recombination occurs. Instead of using the excited charge carriers for a solid state reaction leading to photodecomposition as in the photographic process, the charge carriers are to be captured by the adsorbed reactants, CO₂ and H₂O, for the photochemical surface reaction to commence. The chemical system we utilize must also be able to carry out oxidation and reduction simultaneously just as occurs in the photographic process.

We have been able to produce methane from gaseous CO₂ and H₂O at the surfaces of an oxide-metal sandwich, SrTiO₃-Pt. This was carried on in a 30 torr ambient pressure of the reactants at 300°K while illuminating the oxide by band gap (>3 eV) radiation from a filtered mercury lamp. We have utilized a small surface area (~1 cm²) single crystal oxide sample that was cleaned and well characterized by Auger electron spectroscopy (AES) before and after the experiments. The use of well characterized single crystal surfaces instead of the use of higher surface area powders
was deemed necessary because of the possible side reactions due to contaminants, mainly carbon. The formation of \( \text{CH}_4 \) by the nearly thermo-neutral reaction \( 2\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4 \) has been reported. While large surface area powders or polycrystalline deposits are always carbon contaminated, the small area high purity single crystal sample is readily cleaned by a combination of ion bombardment and chemical treatments before the experiments, thus eliminating the possibility of uncontrolled side reactions. However, as a result of the small surface area of our samples it is more difficult to obtain products in detectable concentrations. The photon-assisted reaction is carried out at near atmospheric pressure in a specially constructed isolation cell that is located in the center of an ultra-high vacuum chamber. When the cell is open the sample could be cleaned in situ by ion bombardment or by chemical treatments at low pressures and the surface composition analyzed by AES. Then the cell is closed around the sample, it is pressurized by the introduction of the reactants (\( \text{CO}_2 \) and \( \text{H}_2\text{O} \)) and the chemical reaction is carried out at any desired surface temperature while the sample is illuminated through a sapphire window.

There are several advantages in performing photochemical reactions at the solid-vapor interface as compared to the solid-liquid interface. The surface composition and its changes, as a result of the reaction, can be analyzed readily by the modern diagnostic techniques of surface science that require high vacuum. Thus, the reaction mechanism can be studied more easily. The absorption of light and the chemical dissolution of the active surface by the electrolyte are absent and the diffusion of reactants and products to and from the surfaces is more rapid.
There are also important advantages in carrying out photosynthesis by the photochemical reactions of H$_2$O and CO$_2$ as compared to the photo-dissociation of water. Although the free energy changes involved in producing some of the small organic molecules, CH$_4$, CH$_3$OH, that may form are larger than for H$_2$ and O$_2$ as shown in Table 1, the free energy changes per electron, $\Delta \varepsilon^0$, for the reduction of CO$_2$ to form these molecules are smaller than $\Delta \varepsilon^0$ for the electrolysis of water (Table 1). It has been shown that, at least for electrochemical reactions, the ease of sequential reduction or oxidation depends on the relative magnitudes of $\Delta \varepsilon^0$ in case of competing reactions. Also, by combined photochemical and catalytic actions of the active surfaces the product distribution in the photosynthetic reaction may be altered.

To verify the elementary steps of the complex photoreaction we have also studied the chemisorption of CO$_2$ and H$_2$O, CO and O$_2$ on stoichiometric SrTiO$_3$(111) crystal surfaces in the dark and in light by a combination of techniques of electron loss spectroscopy (ELS) and ultraviolet photo-electron spectroscopy (UPS). These studies will be described first. Then the photochemical reactions of CO$_2$ and H$_2$O will be discussed as they were carried out using the SrTiO$_3$-Pt sandwiches, along with the "blank" experiments that were carried out to identify more completely the photo-chemically active system.

2. EXPERIMENTAL

2.1 Equipment and Experimental Procedure

All of the chemisorption experiments were performed in a stainless-steel ultra-high vacuum (UHV) chamber evacuated by ion and water-cooled titanium sublimation pumps. The base pressure in the system was in the
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ ) (eV/mole)</th>
<th>( \Delta \varepsilon^\circ ) (eV/electron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 + 2 \text{H}_2\text{O} (g) = \text{CH}_4 + 2 \text{O}_2 )</td>
<td>8.30</td>
<td>1.04</td>
</tr>
<tr>
<td>( \text{CO}_2 + 2 \text{H}_2\text{O} (g) = \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 )</td>
<td>7.15</td>
<td>1.19</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{H}_2\text{O} (g) = \text{H}_2\text{CO} + \text{O}_2 )</td>
<td>5.32</td>
<td>1.33</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{H}_2\text{O} (g) = \text{HCOOH} + \frac{1}{2} \text{O}_2 )</td>
<td>2.98</td>
<td>1.49</td>
</tr>
</tbody>
</table>

**TABLE A3.1.** The standard free energies, \( \Delta G^\circ \), and the free energy changes per electron, \( \Delta \varepsilon^\circ \), for the reduction of \( \text{CO}_2 \) by water to produce a variety of hydrocarbons.
low $10^{-10}$ torr range.

A double pass cylindrical mirror analyzer (CMA) with a coaxial electron gun was used as the primary electron source and electron energy analyzer by which electrons emitted into a conical segment with half angle of 42.3° from the axis of the analyzer were collected. In all Auger electron analysis, the CMA was operated at a constant resolution of 1.5 eV. In this way we could resolve detailed structures of the peaks in the dN/dE Auger spectra, and give reliable estimates of strontium to oxygen and oxygen to titanium ratios under different conditions of surface preparation.

A primary electron beam with energies between 60 - 180 eV was used in the electron energy loss experiments. The electron energy loss spectra (ELS) were obtained either by directly measuring the electron energy distribution N(E) as a function of energy loss or its second derivative $-d^2N/dE^2$. Both methods yielded the same loss peaks except the features in the ELS $-d^2N/dE^2$ spectra were enhanced. The CMA was operated in the retarded mode with pass energy at 50 eV. However, since the primary electron beam was not energy analyzed, the ultimate resolution was limited by the thermal energy spread of the incident electrons which was about 0.5 eV. The energy positions of the loss peaks were independent of incident electron energies in the range of 60-180 eV. All energy loss spectra reported in this paper were obtained with incident energies ~100 eV. The features of these spectra were very surface-sensitive.

In the UPS studies, the cold cathode discharge lamp was operated to generate the HeI spectral line at 21.2 eV. A two-stage differential pumping manifold was employed to minimize the helium leak flow from the discharge lamp into the ultra-high vacuum chamber which maintained a
pressure of $1-2 \times 10^{-9}$ torr during all UPS experiments. The mass spectrometer indicated that the pressure rise was due to the increase of helium partial pressure in the chamber. The specimen was positioned with its surface normal coincident with the axis of the CMA. The angle of incidence of the photons on the specimen was $75^\circ$ from the normal. The analyzer was operated with a constant resolution of 0.35 eV. Typically a spectrum could be obtained within 5 minutes.

The specimen used was a 99.99% undoped strontium titanate single crystal with perovskite structure. Samples of (111) orientation, as determined by the Laue back reflection technique, were cut from this crystal and mechanically polished using $0.05 \mu m$ Al$_2$O$_3$ powders. The specimen was then rinsed in distilled water and mounted on a high density alumina holder, which had a tungsten heater wire located at the back of the sample to allow radiative heating of the crystal. A LEED optics made by Physical Electronics was used to study the surface structure after annealing. Two samples of (111) orientation have been prepared and both gave essentially the same results.

For argon ion bombardment of strontium titanate surfaces, the vacuum chamber was back-filled with argon to a pressure of $6 \times 10^{-5}$ torr. With an accelerating voltage of 2 keV, the ion bombardment could typically deliver an argon ion beam of 20 $\mu$A to the sample surface.

The photoassisted reaction studies were carried out in a specially constructed high pressure-low pressure chamber that is shown in Fig. 1. The UHV system is a commercial Varian surface analysis chamber with low energy electron diffraction, and Auger electron spectroscopy capabilities. The chamber also has a quadrupole mass spectrometer for gas analysis and
Fig. A3.1. Schematic of ultra high vacuum surface analysis chamber equipped with reaction all.
and an ion gun for crystal cleaning. A diffusion pump with cryobaffle were added to the standard ion pump and titanium sublimation pump to handle the extra gas loads when the isolation cell is opened after an experiment. The system base pressure is $\sim 1 \times 10^{-9}$ torr. The isolation cell consists of a cylinder, mounted on a bellows, which can be raised up over the sample by a screw drive. The vacuum seal is made with a gold O-ring. With the cell closed gases are introduced into the cell through connections to an external gas loop. During an experiment the gases are circulated through the cell and the loop, which is external to the vacuum system, by a metal bellows pump. Also in the external loop are: a capacitance manometer (MKS 170M-6B) and the gas sample valve for the gas chromatograph that is equipped with a flame ionization detector (HP 5720A). The sample volume for the gas chromatograph is 0.25 ml. The total volume of the cell plus the external loop is $\sim 90$ ml. This isolation cell allows us to run batch type reactions on well characterized single crystal surfaces.

The sensitivity of the gas chromatograph flame ionization detector system using a chromosorb 102 column for the detection of alkanes and alcohols was excellent, $\sim 10^{-10}$ moles. Thus, less than monolayer quantities ($\sim 10^{15}$ molecules, $10^{-9}$ moles) could be detected. The detection sensitivity is much poorer for $\text{H}_2$, $\text{O}_2$ and HCOOH. The gas mixture could be leaked into a quadrupole mass spectrometer. However, the high concentration of gaseous water and $\text{CO}_2$ yielded enough fragmentation products with the m/e ratio of ionized $\text{O}_2$ and $\text{H}_2$ to eliminate the possibility of their conclusive detection. As a result our system was very poor at detecting $\text{H}_2$, $\text{O}_2$ or HCOOH while it was most sensitive for detecting alkanes and alcohols.
For the photochemical reaction studies, the SrTiO$_3$ crystal samples (1 cm diameter and 1 mm thick disks) were reduced in a hydrogen furnace at 1000°C for 1 hr and then were mounted on a disk of 0.001 inch thick Pt foil and were held in place by two straps of Pt foil (1 mm wide) that were spot welded to the Pt foil backing (Fig. 2). Although the oxide-metal contact was secure it was only a relatively poor mechanical electrical contact. The oxide-metal sandwich so prepared was mounted in the UHV chamber. After cleaning by ion bombardment and annealing by heating in vacuum or in oxygen, an Auger spectrum was taken to determine the surface composition. At this point the isolation cell was closed and pressurize with the reactant gases. The CO$_2$ was Matheson Research Grade and was used without further purification. It contained a small methane impurity which was negligible compared to the methane produced. The pure water was obtained from Scientific Products and was used after several cycles of outgassing by freezing with liquid nitrogen while pumping on the sample. No impurities were detectable in the water by gas chromatography or mass spectroscopy.

Band gap radiation was provided by a 500 watt high pressure mercury lamp in a water cooled housing. Light from the lamp was collimated and focused on the sample with two quartz lenses. An infrared filter consisting of a quartz cell filled with NiSO$_4$ solution was placed between the mercury lamp and the reaction cell, to absorb the heat and transmit the near UV. With this arrangement we were able to obtain a photon flux of $\sim 10^{17}$ photons/sec on the 1 cm$^2$ crystal surface.

In order to obtain quantitative determination of the reaction product concentration, the gas chromatograph was calibrated using pure methane.
Fig. A3.2. Schematic of the SrTiO$_3$(111)-Pt foil sample.
3. RESULTS

3.1. **Selected Properties of SrTiO$_3$**

Stoichiometric SrTiO$_3$ is an insulator, transparent to visible light (band gap 3 eV). It is cubic (perovskite structure) at 300°K, but becomes tetragonal at about 110°K. When the 99.99% undoped strontium titanate obtained from the National Lead Company is reduced by heating in a flow of hydrogen at 1000°K for two hours it turns black and exhibits a dark conductivity of $\sim 1.0$ (ohm-cm)$^{-1}$. Both stoichiometric and reduced SrTiO$_3$ were used in our chemisorption and photochemical reaction studies. The AES and UPS spectra was obtained after ion bombardment at 300°K to remove the impurities (mostly carbon) followed by annealing at 900°K. The AES spectra obtained at 300°K gives peak-to-peak ratios of Sr(65eV)/O(510eV) and O(510eV)/Ti(380eV) 1.5 and 2.0 respectively for both the stoichiometric and reduced samples. Thus, the surface composition appears to be similar as judged by AES. It should be noted that the surface composition of SrTiO$_3$ is temperature-dependent as shown in a recent study.$^{(6)}$ The (111) crystal face exhibits a (1x1) LEED pattern when ordered. Ordering, however, requires heating to 900°K after ion bombardment. While the chemisorption studies were carried out on the ordered (111) surface the chemical reaction studies were carried out mostly on disordered surfaces due to our inability to anneal the oxide surface at high enough temperature on account of poor thermal contacts. The Auger peak-to-peak ratios were not affected by the different degree of ordering on the (111) surface.

The UPS spectra were different for the stoichiometric and reduced (111) surfaces of SrTiO$_3$ as shown in Fig. 3. Both the stoichiometric and
Fig. A3.3. AES and UPS spectra of stoichiometric and reduced SrTiO$_3$. 
reduced crystals have large concentrations of Ti\textsuperscript{3+} ions. This is different from the results found for TiO\textsubscript{2}, where the stoichiometric sample has no observable Ti\textsuperscript{3+} concentration.\textsuperscript{(7)} The transition in the ELS (Fig. 4) due to Ti\textsuperscript{3+} in the reduced SrTiO\textsubscript{3} sample is significantly broadened, indicating the possibility of band formation. There is an additional transition in the UPS (Fig. 3) for the reduced sample near \(\sim 11\) eV indicating differences in the valence band structure.

3.2. Chemisorption of H\textsubscript{2}O, O\textsubscript{2}, CO and CO\textsubscript{2} on the SrTiO\textsubscript{3}(111) Crystal Face in Dark and in Light

When water vapor is introduced into the vacuum chamber at pressures of \(10^{-6}\) torr, adsorption of the oxide surface takes place. Typical exposures were about \(10^4\) Langmuir. The UPS N(E) spectra in the region of the Ti\textsuperscript{3+} transition are shown in Fig. 5. The signal due to the presence of Ti\textsuperscript{3+} ions in the surface decreases upon H\textsubscript{2}O adsorption indicating that much of the Ti\textsuperscript{3+} is oxidized to Ti\textsuperscript{4+} by the adsorbed water molecule. The work function is found to increase by 0.4 eV as a result of water adsorption. This may be due to an increase in the band bending near the surface. This is in striking contrast to water adsorption on TiO\textsubscript{2} which causes a decrease in the work function of 0.8 eV.\textsuperscript{(7)}

When water adsorption is followed by illumination of the surface with band gap radiation the Ti\textsuperscript{3+} signal is only partially regenerated as shown in Fig. 5. The work function is not affected.

The UPS difference spectra for water adsorption on SrTiO\textsubscript{3}(111)-(1×1) and a TiO\textsubscript{2} surface which was reduced by Ar\textsuperscript{+} bombardment are shown in Fig. 6. The two spectra are quite similar but they are quite different
Fig. A3.4. ELS spectra in the region of the Ti$^{3+}$ transition for stoichiometric and reduced SrTiO$_3$. 
Fig. A3.5. UPS N(E) spectra in the region of Ti$^{3+}$ transition for H$_2$O absorbed on SrTiO$_3$, before and after illumination.
Fig. A3.6. UPS difference spectra for H₂O adsorbed on TiO₂ reduced by Ar⁺ bombardment and on stoichiometric SrTiO₃.
from that of undissociated water.\textsuperscript{(7)} Recent calculations by Tsukada et al. indicate that OH\textsuperscript{−} may be formed on the reduced TiO\textsubscript{2} surface.\textsuperscript{(8)} From our results it appears the water adsorbs dissociatively on surfaces of TiO\textsubscript{2} and SrTiO\textsubscript{3} which have significant Ti\textsuperscript{3+} concentrations. Thus water adsorbs dissociatively on reduced TiO\textsubscript{2} and both stoichiometric and reduced SrTiO\textsubscript{3}. In the process of dissociative adsorption of H\textsubscript{2}O the Ti\textsuperscript{3+} sites are oxidized to Ti\textsuperscript{4+}.

Oxygen chemisorption of the SrTiO\textsubscript{3}(111) crystal face after exposure to \(5 \times 10^{4}\text{ L}\) increases the work function by \(\Delta\phi = 0.9\text{ eV}\). The Ti\textsuperscript{3+} signal is completely removed by chemisorbed oxygen. This is shown in the UPS N(E) spectra that is displayed in Fig. 7. Illumination of the surface with bandgap radiation, after O\textsubscript{2} adsorption, regenerates a significant amount of Ti\textsuperscript{3+} as shown in Fig. 7. However, upon illumination of the O\textsubscript{2} covered surface the work function is reduced by only 0.2 eV which is still 0.7 eV greater than the work function of the clean stoichiometric sample. The fact that the work function does not return to the value of the clean stoichiometric sample upon illumination indicates that not all the adsorbed O\textsubscript{2} is removed by photodesorption.

Both CO and CO\textsubscript{2} give rise to the same UPS difference spectra when adsorbed on the SrTiO\textsubscript{3} surface. The spectrum is shown in Fig. 8. The measurements were taken after exposure on the surface to \(5 \times 10^{4}\text{ L}\) of these gases. The work function is found to increase by 0.3 eV on adsorption of CO\textsubscript{2}. The Ti\textsuperscript{3+} signal is significantly decreased. On illumination there is not noticeable change in either the work function or the Ti\textsuperscript{3+} signal.

Upon heating the sample after CO adsorption only CO\textsubscript{2} is observed
Fig. A3.7. UPS N(E) spectra in the region of the Ti$^{3+}$ transition for O$_2$ adsorbed on SrTiO$_3$, before and after illumination.
Fig. A3.8. UPS difference spectra for CO$_2$ and CO adsorbed on stoichiometric SrTiO$_3$. 

UPS for SrTiO$_3$ (III) - (1×1) + 5×10$^4$ CO
\[ \Delta \phi = +0.5 \text{ eV} \]

UPS for SrTiO$_3$ (III) - (1×1) + 5×10$^4$ CO$_2$
\[ \Delta \phi = +0.4 \text{ eV} \]
to desorb, indicating that CO may be efficiently converted to CO₂ on the oxide surface.

There is considerable experimental evidence indicating that CO is readily oxidized to CO₂ over several transition metal oxide surfaces in addition to SrTiO₃.⁹ An oxygen ion from the crystal lattice is likely to be used for this purpose. The reduction of CO₂ to CO that is commonly observed on many transition metal surfaces does not appear to occur on the oxide surface. Another reaction that converts CO to CO₂ is its disproportionation 2CO → C + CO₂ that may also occur. We cannot rule out this reaction as a possible path to convert CO to CO₂, although we do not see the accumulation of much carbon on the oxide surface. During the photosynthetic reaction in the presence of H₂O, CO₂ and light some carbon does accumulate on the stoichiometric SrTiO₃ surface that is detectable by AES. Carbon is never found to accumulate on the reduced SrTiO₃ that presents an oxygen-deficient surface to the incoming reactants. Since the photochemical activity of the reduced and oxidized surface is nearly identical at 300°K, the reaction that converts CO₂ to CO does not appear to be an essential chemical route in the formation of methane.

In summary, H₂O dissociates at least partly on adsorption as indicated by the electron spectra and oxidizes Ti³⁺ to Ti⁴⁺ in the process. Ti³⁺ is only partly regenerated by bandgap radiation. Oxygen adsorbs in several states on the surface. It desorbs from the state that is associated with the oxidation of Ti³⁺ to Ti⁴⁺ and the Ti³⁺ sites are regenerated. Other types of chemisorbed oxygen remain on the surface during illumination, as indicated by the work function change. CO and CO₂ give rise to the same changes in the electron spectra indicating that
they form the same surface species on the oxide surface. It appears that CO is converted to CO₂ by a slow surface reaction.

3.3. **Chemisorption of H₂O, O₂, CO and CO₂ on Pt Surfaces**

Water is known to chemisorb rather poorly on Pt surfaces at low pressures. It remains molecular on the surface and is bound only weakly. Evacuation of the reaction chamber after exposure of the Pt to high pressures (several torr) of water resulted in total removal of the water at room temperature, clearly indicating weak binding. There was no evidence for water dissociation on the Pt surface even at these higher pressures.

Oxygen chemisorbs on Pt single crystal and polycrystalline foil surfaces at low and high pressures. There is evidence for the presence of chemisorbed oxygen as well as the formation of oxide under appropriate experimental conditions.\(^{[10]}\) Under conditions of the photochemical reaction studied here, oxygen should mostly be in the chemisorbed state.

Chemisorbed oxygen also interacts strongly with carbon or adsorbed CO on the Pt surface. The kinetics of oxidation of C or CO on Pt have been studied extensively.\(^{[11]}\)

CO chemisorbs on Pt with a sticking probability of unity even at very low pressures (~10⁻⁹ torr). It stays molecular but strongly bound on the metal and it exhibits many binding states with distinguishable heats of adsorption that vary from 32 to 14 kcal/mole.\(^{[12]}\) Only surface kink sites will dissociate CO to carbon and oxygen on Pt as indicated by photoelectron spectroscopy studies.\(^{[13]}\) Since the concentration of kink sites is a small fraction of the total number of surface sites, most of
CO adsorbed on the Pt surface should remain molecular.

CO$_2$ adsorbs poorly with a low sticking probability on Pt at low pressures (~$10^{-6}$ torr). At pressures of several torr that are utilized in our photochemical studies, CO$_2$ adsorbs as indicated by subsequent thermal desorption. Only CO$_2$ is observed in our thermal desorption experiments. No carbon buildup on the Pt is observed by AES after exposure to 15 torr CO$_2$ in the dark. Thus it appears that CO$_2$ remains largely molecular on the Pt surface in the absence of hydrogen and light and is weakly bound. We find no evidence for the dissociation of CO$_2$ to CO and O.

3.4. The Photochemical Reaction of Gaseous H$_2$O and CO$_2$ to Produce CH$_4$ over SrTiO$_3$-Pt Sandwiches

The SrTiO$_3$-Pt sandwich, after cleaning by ion bombardment and heat treatments, is analyzed by AES and then enclosed in the isolation cell. The cell is filled with 15 torr H$_2$O and 15 torr CO$_2$. The gas composition is analyzed by the gas chromatograph and then the experiment commences. The oxide side of the sandwich is illuminated by light of band gap or larger energy using a 500 watt Hg lamp. A NiSO$_4$ filter is used to screen out the infrared radiation to avoid heating the sample. The thermocouple that is attached to the sandwich registers less than 10° temperature rise throughout the experiments at 300°K.

Methane gas is produced for the first 10 minutes of the illumination and is readily detected by the chromatograph. The number of methane molecules formed is plotted as a function of time in Fig. 9. The initial rate of formation is $2 \times 10^{14}$ molecules/min, which corresponds to a quantum yield of 1 molecule of methane per $10^4$ photons. The total amount of
Fig. A3.9. Methane production as a function of time of illumination of the SrTiO$_3$-Pt sandwich in the presence of CO$_2$ and H$_2$O.

Initial Rate $\sim 2 \times 10^{14}$ molecules/minute

$P_{H_2O} = 17$ torr

$P_{CO_2} = 15$ torr
methane formed is \( \sim 10^{15} \) molecules, or \( \sim 10^{-9} \) moles; that corresponds to about one monolayer. The production of methane slows down with time and then stops after 10 minutes. This reaction inhibition is due to a tenacious "poison" since pumping out the reactants and reintroducing fresh \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) does not regenerate the chemical activity of the surfaces. The photo-chemical activity is regenerated, however, by renewed ion bombardment and annealing, i.e., complete cleaning of the metal and oxide surfaces. AES indicates the buildup of a monolayer of carbon on the \( \text{Pt} \). There is a thermal generation of methane when a reduced \( \text{SrTiO}_3 \) sample is used in the oxide-metal sandwich. Upon heating to \( 600^\circ\text{K} \) in the dark, a monolayer \( \text{CH}_4 \) can be generated just as in light at \( 300^\circ\text{K} \). In both cases \( \text{CH}_4 \) production stops after the formation of about a monolayer. It appears that the poisoning reaction is the same in the light-driven and thermally-driven reactions, and we detect a monolayer deposit of carbon on the \( \text{Pt} \) in both cases. Substitution of CO for \( \text{CO}_2 \) in the reaction mixture does not increase the methane yield. This observation combined with the evidence favoring \( \text{CO}_2 \) in the \( \text{CO}/\text{CO}_2 \) equilibrium over oxides seems to rule out \( \text{CO} \) as an important intermediate in the reaction paths of methane formation.

The following experiments were carried out to prove that \( \text{CH}_4 \) production was indeed the property of the metal-oxide contact. The following experiments all produced no detectable amounts of \( \text{CH}_4 \):

1. The \( \text{SrTiO}_3\)-\( \text{Pt} \) sample with only \( \text{CO} \) (no \( \text{H}_2\text{O} \)) in the presence of light and by heating the sample to \( 450^\circ\text{K} \).

2. The \( \text{SrTiO}_3 \) crystal without the \( \text{Pt} \) foil using \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) mixtures and illumination.
3. The Pt foil alone using CO\textsubscript{2} and H\textsubscript{2}O mixtures, both with illumination, and by heating the Pt foil to 450°K.

4. The SrTiO\textsubscript{3}-Pt sample in a CO\textsubscript{2} and H\textsubscript{2}O mixture using illumination with light of energy less than the band gap of SrTiO\textsubscript{3} (light with energy less than the band gap was obtained by placing a Corning glass filter between the NiSO\textsubscript{4} solution filter and the reaction cell).

The last experiment indicates that band gap radiation is necessary for the photoassisted production of CH\textsubscript{4} from CO\textsubscript{2} and H\textsubscript{2}O. This is consistent with the observed necessity for band gap radiation to dissociate H\textsubscript{2}O in the electrochemical cell experiments. These experiments do establish that the photon-assisted reaction is a property of the oxide-metal contact system. It appears that the major obstacle in producing more methane may be the deposition of a monolayer of carbon on the Pt surface that seems to block the chemical reaction.

4. DISCUSSION

There are several important observations that help us to understand the photon-assisted process leading to the formation of CH\textsubscript{4} from CO\textsubscript{2} and H\textsubscript{2}O:

1. Both the oxide SrTiO\textsubscript{3} and the metal are needed to observe the production of methane.

2. The photochemical reaction poisons in 10 minutes at 300°K in the reactant mixture. Surface analysis indicates carbon deposition at the Pt surface. The reduced oxide surface remains clean while there is a fractional monolayer of carbon
detectable on the stoichiometric SrTiO$_3$. A thermal reaction exists which also produces CH$_4$.

3. Water adsorbs dissociatively on the oxide surface while it remains molecular on the Pt surface. CO is oxidized to CO$_2$ on the oxide surface. $O_2$ chemisorbs on both oxide and metal surfaces. Part of the chemisorbed oxygen that is utilized for the oxidation of Ti$^{3+}$ ions to Ti$^{4+}$ photodesorbs and the Ti$^{3+}$ sites are regenerated.

4. Band gap radiation is necessary to carry out the photochemical reaction.

5. The energy needed to carry out the production of methane from CO$_2$ and H$_2$O is much larger than the band gap of SrTiO$_3$, indicating that the process must occur in a stepwise manner.

The presence of the metal, Pt in our case, appears to be necessary for both catalytic and electrical reasons. Separation of the photon-generated electrons and holes at the oxide surface is likely to be enhanced by the metal-oxide contact. Platinum appears to participate in the CO$_2$ reduction process, most likely through its hydrogenation of the molecule or the reaction intermediates.

While the chemisorption studies indicate that H$_2$O dissociates on the oxide surface, there is little information at this point on the mechanism of CO$_2$ reduction. Since carbon accumulates at the metal surface it appears that at least part of the carbon cycle involved in the reduction of CO$_2$ to CH$_4$ takes place at the metal surface. One possible reduction scheme would be the conversion of CO$_2$ to CO and then into dissociated oxygen and carbon. The rehydrogenation of C to CH$_4$ that is obtained by the dissociation of CO on Ni, Fe and Rh surfaces appears to
be the dominant mechanism for methanation from CO and H₂ on these transition metal surfaces. Pt, however, dissociates CO only at kink sites that are present in low surface concentrations, and this process is not likely to account for the formation of the carbon monolayer. Moreover, when CO was substituted for CO₂ the photochemical reaction was not enhanced and there is evidence for the oxidation of CO to CO₂ at the SrTiO₃ surface. Thus we are tempted to rule out this reduction scheme.

A more likely reaction path leading to CH₄ formation may be the hydrogenation of CO₂ to formic acid (HCOOH) or formaldehyde (H₂CO) with further reduction to CH₄. Future studies will be directed toward verifying the reaction intermediates—the carbon cycle leading to CH₄ production.

We may suggest a tentative reaction sequence leading to the formation of CH₄ from CO₂ and H₂O on the oxide-metal sandwich. Water adsorbs dissociatively on the SrTiO₃ surface. The photoelectrons and holes produce H atoms or H⁺ ions and O₂ molecules. While O₂ photodesorbs, at least in part (there is evidence from our UPS studies that not all of the chemisorbed oxygen is removed by photodesorption), the H atoms or H⁺ ions migrate onto the Pt surface where the hydrogenation of CO₂ and subsequently that of the reaction intermediates occur.

It is notable that CH₄ may be produced in the dark over reduced SrTiO₃-metal sandwiches. Since the poisoning mechanism seems to be the same as during the photon-assisted process, further investigations may permit the steady state production of methane in this circumstance as well. Under certain conditions it can be advantageous to carry out this reaction in the thermal mode instead of under illumination. An added problem, of course, is the need to stabilize the nonstoichiometric
composition in the near surface region. Our UPS studies revealed the likely presence of a Ti$^{3+}$ impurity band that appears to be the cause of the thermally generated electrons and holes that provide the driving force for this thermodynamically uphill reaction.

There are many future experiments necessary to verify the mechanism of this photosynthetic reaction over the oxide-metal contacts. The role of the metal, electronic or catalytic, should be verified. The effect should be tested using other oxides and other metals as the photochemistry may be markedly changed in this way.

It is likely that other molecules, in addition to methane, may also be produced using other appropriate oxide-metal contacts, light of suitable wavelength, and gas mixtures of CO$_2$, H$_2$O and N$_2$. Indeed, light-assisted reactions over oxide-metal contacts may provide a new route for the production of many different small molecules.

Since the formation of CH$_4$ from CO$_2$ and H$_2$O is obviously a multi-step process, semiconductors with smaller band gaps should not be ruled out as photoassistant agents in these types of reactions.
APPENDIX 3: REFERENCES

11. a. H. Hopster, H. Ibach and G. Comsa, J. Cat. 46, 37 (1977);  
APPENDIX 4: ENERGY BAND DIAGRAM OF SEMICONDUCTOR
SURFACE SPACE CHARGE REGION

The above figure shows the schematic energy band diagram of a semiconductor surface space charge region after different surface treatments, where $\chi_{sc}$ is the semiconductor electron affinity; $\phi_{sc}$ is the semiconductor work function; $\phi_B$ is the barrier height for conduction electron to reach the surface; $\Delta V_B$ is the change of band bending; and $\Delta X$ is the interface dipole energy corresponding to the change of electron affinity after surface treatments (e.g., ion sputtering).

The region where electron affinity is changed by ion sputtering is illustrated proportionally larger to display dipole effects. The relation between change of work function $\Delta \phi$, and $\Delta X$, $\Delta V_B$ can be expressed according to the following equation

$$\Delta \phi = \Delta X + \Delta V_B$$

i.e., both the band bending $\Delta V_B$ and interface dipole potential $\Delta X$ change the surface work function and thereby contribute to the barrier height $\phi_B$. Experimentally, the surface work function $\phi$ can be measured according to the expression $\phi = h \nu (21.2eV) - (\text{width of photoelectron})$.
energy distribution curve), and $qV_B$ can be obtained from the change of energy separation between $E_F$ and surface valence-band edge in the photo-electron energy distribution.
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