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UPS AND XPS STUDIES OF THE CHEMISORPTION OF O₂, H₂ AND H₂O ON REDUCED AND STOICHIOMETRIC SrTiO₃(111) SURFACES. THE EFFECTS OF ILLUMINATION

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Abstract

About one monolayer of Ti$^{3+}$ species is detectable at the surface of reduced SrTiO$_3$(111) single crystals by XPS and UPS. O$_2$, H$_2$, and H$_2$O have been adsorbed in the dark and the decrease on the concentration of the Ti$^{3+}$ species has been monitored as a function of the gas exposures. Subsequent band gap illumination partially restores the Ti$^{3+}$ initial concentration in the cases of O$_2$ and H$_2$ exposures but not in the case of H$_2$O. The Ti$^{3+}$ photogeneration on the oxygen covered surface is associated with oxygen photodesorption as indicated by XPS and UPS. UPS measurements give evidence for surface hydroxylation resulting from water and hydrogen adsorption.

The activity of the stoichiometric SrTiO$_3$(111) crystal face for O$_2$ and H$_2$ adsorption is very low when compared with the reduced SrTiO$_3$ samples.

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1. Introduction

The photodecomposition of water into hydrogen and oxygen is a promising means of converting solar energy to a storable fuel. Strontium titanate (SrTiO$_3$) is one of the materials that carries out this reaction when illuminated by band gap radiation (3.2 eV) in the photoelectrochemical cell without any applied external potential (1). The reactivity and catalytic properties of solid surfaces have been found to be closely related to their structural and electronic properties, and it is essential to undertake surface studies to explore this correlation for SrTiO$_3$ that is so active for water photolysis. Several papers dealing with various surface properties of SrTiO$_3$ single crystals and other titanium oxides have been published (2-6); but there is little known of the correlation of its structure, composition and electronic properties to the interaction with H$_2$O, H$_2$ and O$_2$ in the dark and under illumination. These are conditions utilized during the photochemical dissociation of water.

In this paper we report the results of photomission studies (UPS, XPS) of clean SrTiO$_3$(111) surfaces, of the adsorption of O$_2$, H$_2$ and H$_2$O in the dark and of the influence of band gap illumination on the chemisorbed layers.

Henrich et al. (3,6) have examined the effect of the defects introduced by ion sputtering on the surface electronic structure and reactivity of SrTiO$_3$ and TiO$_2$. They conclude that the reactivity of these surfaces is closely related to the presence of such surface defects. Wolfram et al. (7) have carried out surface band
calculations of SrTiO$_3$ showing the existence of d-like surface states and their importance in surface chemical reactions. Boonstra and Mutsaers (8) show that the surface photoactivity for a TiO$_2$ powder is proportional to the number of hydroxyl groups on the surface. In the report we present new information on the role of the Ti$^{3+}$ species and show evidence for surface hydroxylation. We have performed UPS and XPS studies on a hydrogen reduced SrTiO$_3$(111) crystal that had been Ar sputtered and annealed at moderate temperature and we have also studied a stoichiometric SrTiO$_3$(111) crystal that was annealed at high temperature in ultra-high-vacuum for a few minutes. At the surface of the reduced oxide a high concentration of Ti$^{3+}$ was detected by XPS and UPS. Exposure to oxygen caused a large decrease on this Ti$^{3+}$ concentration. Subsequent band gap illumination partially restored the initial concentration of Ti$^{3+}$. This photoregeneration of Ti$^{3+}$ ions was accompanied by photodesorption of oxygen. Water and hydrogen exposures gave rise to the formation of hydroxyl species on the surface as shown by UPS. The stoichiometric crystal surface exhibits no visible amount of Ti$^{3+}$. This surface is very inert to H$_2$ and O$_2$ exposure and shows no photoactivity. Comparison of these two extremes of surface chemical activities for the reduced and stoichiometric oxides clarifies the roles of Ti$^{3+}$ and surface hydroxylation during the photochemical dissociation of water.
2. Experimental

Two SrTiO$_3$ single crystals supplied by National Lead were used in this study. Both were of (111) orientation (determined by Laue X-ray diffraction). One was reduced in a H$_2$ furnace for several hours at 700°C resulting in a black colored sample. The other, a transparent sample of high resistivity, received no hydrogen or heat pre-treatment. We will refer to the first one as reduced and to the second one as stoichiometric. Due to the high electrical resistivity of the stoichiometric crystal, it charged up in the electron and photon beams. This effect could be minimized by heating it at ~700°C for several minutes in ultra-high-vacuum (U.H.V).

The U.H.V. system, electron analyzer, UPS and AES equipments have been described in detail elsewhere (5). The X-ray source was a Physical Electronics model 1000 with a Mg anode operated tipically at 300 watts. The base pressure of the system was in the low 10$^{-10}$ torr range, and less than 1 x 10$^{-9}$ torr during the UPS experiments. This increase of the base pressure was due to the helium from the uv source.

Band gap radiation was provided by a 500 watt high pressure mercury lamp that was placed in a water cooled housing. Light from the lamp was focussed and collimated with a fused quartz condenser lense. A 6 cm thick water filled quartz filter was used to absorb infrared radiation. A corning glass filter 7-51 (uv transmitting, absorbing in the visible) was also used to minimize the heating effects while transmitting band gap radiation. The light beam was introduced into the vacuum system through a sapphire window. The
photon flux with energy equal or greater than the crystal's band gap (3.2 eV) was estimated to be in the range of $10^{14} - 10^{16}$ photons per cm$^2$. Instead of the 7-51, a 3-74 filter was employed in the experiments where we were interested in illuminating the crystal with sub band gap radiation. Due to the severe electron beam damage observed on the crystals, the Auger spectra were recorded at the end of experiments. Care was taken that prior to the photoemission measurement the crystal were not electron beam irradiated. Blank experiments were performed in order to determine possible damage caused by the HeI (21.2 eV) or X ray (1253.6 eV) beams. No damage or spurious effects were observed. While obtaining the UPS spectra the electron analyzer was operated at resolutions of 0.2 or 0.1 eV. In the XPS spectra the resolution was 0.7 or 0.35 eV. We refer the electron binding energies to the crystal Fermi level in the UPS spectra and to the vacuum level in XPS. In this second case, since no absolute calibration was performed, the absolute binding energy values are only approximate (±1-2 eV). The Auger spectra were taken with the analyzer retarding mode at resolution of 1.5 eV. Spectra were recorded in the dN/dE mode using a modulation potential of 1 or 2 volts. The oxide samples could be readily cleaned, and in only a few cases were small carbon traces present in the Auger spectra after an experiment. The ion bombardement gun was operated at 1.5 kV of accelerating voltage. The Ar beam current was of a few μA onto the crystal and the usual sputtering time was 5 minutes.
3. Results

3.1. The clean crystal surface of reduced SrTiO$_3$(111). AES, XPS and UPS studies.

Figure 1 shows AES, XPS and UPS spectra obtained when the reduced SrTiO$_3$(111) crystal was Ar sputtered, annealed at ~200° C for a few minutes and cooled to room temperature. No ordered LEED pattern was visible. In the following discussion we will refer to the surface with this treatment as the clean reduced surface. For this surface the Auger peak to peak ratios are Sr(65 eV)/O(510 eV) and O(510 eV)/Ti(380 eV) 6.1 and 1.7 respectively. When compared with data reported for a stoichiometric crystal (5), the O/Ti ratio remains approximately the same but the Sr/O ratio is significantly larger for our reduced crystal. The UPS spectrum shows the following features: At ~0.8 eV below the Fermi level there is an emission that corresponds to the 3d electronic level in Ti that is partially occupied when Ti$^{+3}$ ions are present on the surface (2,3). Between 4 and ~9 eV there are two overlapping O 2p levels corresponding to the octahedral symmetry of the oxygen ions in the perovskites (7,9). At ~12 eV superimposed on the secondary electron emission tail we observe a peak that can be associated with the presence of hydroxyl groups at the surface, as will be discussed later. From the low-energy cutoff of the UPS spectrum a work function of ~1.9 eV is obtained.

The Ti 2p XPS emission peaks shown in Fig. 1 correspond to the photoelectrons from Ti 2p$_{3/2}$ at 461 eV and Ti 2p$_{1/2}$ at 468 eV. At about 2.5 eV from the Ti 2p$_{3/2}$ peak on the low binding energy
side, there is a visible shoulder that corresponds as we shall show later, to the Ti$^{3+}$ 2p$_{3/2}$ emission. The O(1s) XPS peak at 532 eV is asymmetric (the left side is wider than the right side), indicating that at least two oxygen species are present in the near surface region.

3.1.1. Ti$^{3+}$ species. Location and concentration.

The magnitude of the Ti$^3$ emission is very sensitive to the oxygen exposure. If the clean reduced surface is exposed to 2 L of oxygen, the intensity of the UPS Ti$^{3+}$ emission (measured as the area under the 0.8 eV peak with a linear background subtracted) decays to about one half of its initial value. This large decrease as a result of such a small exposure shows that the Ti$^{3+}$ ions are a surface species.

We shall now show that the shoulder of the Ti 2p$_{3/2}$ XPS peak mentioned above corresponds to the Ti$^{3+}$ 2p$_{3/2}$ emission. In Fig. 2a we show the Ti 2p XPS peaks from the clean reduced surface. Upon deconvoluting the Ti 2p$_{3/2}$ portion of the spectrum we obtain two peaks. The main peak at 461 eV corresponds to the 2p$_{3/2}$ emission of Ti$^{4+}$ which is the majority species in the crystal. The low binding energy shoulder consists of a peak with intensity 0.34 relative to the main Ti$^{4+}$ peak and located at ~3.3 eV. This shift agrees qualitatively with previously reported data on titanium suboxides (10).

In Fig. 2b we show the Ti XPS emissions after 0.5 L of oxygen exposure. The intensity of the shoulder has been greatly diminished. This parallel behavior with the Ti$^{3+}$ UPS emission enables us to
confirm that this low binding energy shoulder corresponds to the Ti$^{3+}$ 2p$_{3/2}$ emission. In Fig. 2c we show the difference spectrum due to the oxygen exposure. We observe that the decrease of the Ti$^{3+}$ 2p$_{3/2}$ emission, represented by a negative peak in the difference spectrum, is accompanied by an increase of the intensity of the main Ti$^{4+}$ 2p$_{3/2}$ emission being both of approximately the same intensity. The effect of the oxygen adsorption is therefore the oxidation of Ti$^{3+}$ to Ti$^{4+}$. We can estimate the concentration of Ti$^{3+}$ species on the clean reduced surface from the ratio of the intensities of Ti$^{3+}$ and Ti$^{4+}$ emissions in the XPS spectrum. Let us take as the attenuation factor $e^{-nd/\lambda \cos \theta}$ for the intensity of Ti 2p photoelectrons that must travel n crystal layers in order to leave the solid. $d = 1.13\text{Å}$ is the distance between two consecutive crystal layers (the packing sequence in the (111) direction for the SrTiO$_3$ perovskite is ...ABAB... where A denotes a titanium layer and B an oxygen-strontium layer), $\lambda \approx 15\text{Å}$ is the photoelectron mean free path for inelastic scattering, and $\theta = 42^\circ$ is the acceptance angle of the electron analyzer. If we were to assume that the first Ti layer (the closest to the surface) consists exclusively on Ti$^{3+}$ ions and that the remaining Ti layers are comprised of Ti$^{4+}$ ions only, we would obtain a Ti$^{3+}$ to Ti$^{4+}$ emission ratio of 0.23. This is considerably smaller than the 0.34 experimental value. So we must conclude that the Ti$^{3+}$ species is present in the surface region in an amount exceeding one monolayer. Assuming that the Ti$^{3+}$ concentration $\theta$ decreases exponentially with distance from the surface...
and that the first Ti layer consists of Ti$^{3+}$ only we can write
\[ \theta_i = e^{-k(i-1)} \quad i = 1, 2, 3, \ldots \]
where \( i \) denotes Ti layers and \( k \) is a concentration gradient parameter that can be adjusted. Using this model, the experimental Ti$^{3+}$/Ti$^{4+}$ XPS emission ratio implies a \( k \) value of 1.13. Roughly speaking we can then conclude that on the clean reduced surface the percentage of total titanium present at Ti$^{3+}$ is 100% for the first layer, 30% for the second, 10% for the third etc.

3.1.2. Effects of O$_2$, H$_2$, and H$_2$O adsorption on the Ti$^{3+}$ species in the dark and in light

The clean reduced surface was exposed to O$_2$, H$_2$, and H$_2$O in dark up to $2 \times 10^3$ Langmuirs, and the intensity of the Ti$^{3+}$ UPS emission was monitored as a function of the gas exposure. After the exposure the system was evacuated and the surface was irradiated with light of band gap energy. The intensity of the Ti$^{3+}$ emission was then monitored as a function of the illumination time. Figure 3 shows the results obtained. In the case of O$_2$ exposure we observed a very strong initial decrease in the Ti$^{3+}$ concentration in dark. After the gas exposure the Ti$^{3+}$ intensity was 10% of its initial value. Subsequent illumination with band gap energy light partially restored the Ti$^{3+}$ signal up to a 20% of its initial value. H$_2$ and H$_2$O exposures in the dark also diminished the Ti$^{3+}$ concentration, but the changes were less dramatic compared to that during the oxygen adsorption for which the initial decrease in Ti$^{3+}$ concentration was \(~8\) times larger. After hydrogen exposure a 65% reduction of the
$\text{Ti}^{3+}$ initial signal was observed. The signal was regenerated by illumination up to a 50% of its initial value. In the water adsorption experiment we observed a 40% decrease in $\text{Ti}^{3+}$ after the exposure and no $\text{Ti}^{3+}$ photoregeneration. To summarize, $\text{Ti}^{3+}$ photoregeneration was observed when the clean reduced surface was exposed to oxygen or hydrogen but not when was exposed to water.

3.1.3. Oxygen adsorption in the dark monitored by the oxygen photoemission spectra. Effect of illumination.

Figure 4 trace a represents the XPS O(1s) emission from the clean reduced surface. In trace b the same spectrum after 100 L of oxygen exposure in dark is displayed. The area under the peak has increased slightly. This increase is clearly visible in trace c which shows the difference spectrum between b and a. Curve c shows a positive peak with an intensity proportional to the amount of oxygen adsorbed. Trace d shows the difference spectrum after 100 minutes of band gap illumination. It is essentially flat, indicating that the adsorbed oxygen has disappeared from the surface as a consequence of the illumination. We interpret this effect as a photodesorption of the adsorbed oxygen in agreement with several recent papers that report oxygen photodesorption from $\text{TiO}_2$ (11,12) and ZnO (13,14). It should be pointed out that the oxygen photodesorption is wavelength dependent. Illumination by light of less than band gap energy did not induce any photodesorption of the adsorbed oxygen.

The photodesorption of oxygen is also visible in the UPS spectrum. In the upper curve of Fig. 5 we show the UPS difference
spectrum that corresponds to a $2 \times 10^3$ L O$_2$ exposure in the dark on the clean reduced surface. The reduction of the Ti$^{3+}$ emission upon oxygen adsorption is readily detectable as a negative peak below the Fermi level. Three oxygen-induced emissions are seen at 4.5, 5.8 and 11.4 eV with relative intensities and positions that are in rather good agreement with previously published data on SrTiO$_3$(100) (6).

The lower curve in Fig. 5 corresponds to the oxygen and adsorption-induced spectrum after 40 minutes of band gap illumination. We observe no changes in either the peak positions or in the peak shapes in the spectrum. However, there is a decrease of about 50% on the intensities of all the peaks indicating that about one half of the adsorbed oxygen has photodesorbed.

Oxygen adsorption caused changes in the work function $\phi$. We observed an increase with the oxygen exposure, reaching the value of $\Delta \phi = +0.8 \pm 0.1$ eV for $2 \times 10^3$ L. Subsequent illumination causes a small decrease to $\Delta \phi = 0.6 \pm 0.1$ eV.

3.1.4. UPS spectra of the water and hydrogen exposed oxide surfaces in the dark and upon illumination

In this section we present evidence for the appearance of surface hydroxyls as a result of water or hydrogen adsorptions in the dark on the clean reduced SrTiO$_3$ surface or as a result of band gap illumination of the clean reduced surface.

The upper curve in Fig. 6 shows the UPS spectrum of a thoroughly outgassed NaOH pellet. It consists of three peaks separated by ~2.4
and 5.3 eV. (Charging effects precluded absolute determination of the photoelectron energies.) This UPS spectrum is due to the OH$^-$ species since the binding energy for 2p sodium electrons is about 30 eV while the HeI exciting photons have an energy of only 21.2 eV. The Auger spectrum of the NaOH pellet exhibited the 0 510 eV and Na $\sim$995 eV peak with a small C peak present. Figure 6 also shows the UPS spectrum due to a $\sim$1 micron thick NaOH film on the reduced SrTiO$_3$ crystal. This spectrum is essentially identical to that from the NaOH pellet except for a superimposed background. The Auger spectrum of this film showed a chlorine peak which could not be eliminated about one-third of the size of the oxygen peak and traces of carbon. In the upper curve of Fig. 7 we present again the UPS N(E) spectrum of the NaOH film. The second curve in Fig. 7 corresponds to the UPS difference spectrum due to a 2000 L water exposure on the clean reduced SrTiO$_3$ surface. It consists of four peaks at 4.6, 6.5, 11.8 and 16.4 eV. By comparing the water induced UPS spectrum with the N(E) spectrum of the NaOH film, we observe good general agreement in the distances between the peaks and in the shape of the curves. We may notice however two discrepancies. The first is the position of the more strongly bound peak at 16.4 eV, and the second is the 4.6 eV water induced-peak which is not visible in the NaOH film spectrum. The $\sim$16 eV region in the UPS spectrum of the oxide surface is superimposed on an intense secondary emission background that makes the determination of the peak location less precise. The 4.6 eV peak
may be due to the splitting of the O (2p) levels of the lattice oxygen ions due to its octahedral symmetry in the perovskite structure. In summary we believe that the similarity between the water induced UPS spectrum on the clean reduced SrTiO$_3$ surface and the spectrum of the NaOH film, allows us to conclude that the water vapor adsorption gives rise to a hydroxyl species on the oxide surface (15). Electron stimulated desorption studies by Knotek et al. (16) show a large increase in the OH$^+$ desorption yield when a TiO$_2$ (100) surface is exposed to 300 L of water.

In the third curve of Fig. 7 we show the UPS difference spectrum due to an 2000 L H$_2$ exposure of the clean reduced oxide surface. In the fourth curve we show the difference spectrum obtained when the clean reduced surface is illuminated, i.e. (band gap illumination of the clean reduced SrTiO$_3$ surface)-(clean reduced SrTiO$_3$ surface). Both spectra are virtually identical with the water-induced spectrum, indicating that by adsorbing hydrogen in the dark or by simply illuminating the clean reduced crystal surface we obtain surface hydroxyls.

Below the Fermi level in the water and hydrogen induced spectra we observe a negative peak corresponding to the depletion of the Ti$^{3+}$ species discussed in Section 3.1.2. this is not visible in the light-induced spectrum. Separate experiments confirmed this point by showing no changes in the Ti$^{3+}$ UPS emission due to the band-gap illumination of the clean reduced surface. Since the peak intensities in the three lowest curves in Fig. 7 are roughly equal, the hydroxyl concentration resulting of the three experiments must be rather
similar. Although 100 minutes of band gap illumination is required to produce $\Delta N$ spectra comparable in magnitude to those induced by $H_2$ or $H_2O$ adsorption, definite photoeffects can be seen after only 10 minutes of irradiation. If after the hydrogen exposure of the clean reduced surface in the dark (Fig. 7, 3rd curve) we irradiate it with band gap light for 100 minutes, no changes are visible in the UPS difference spectrum. Essentially the same results are obtained in the case of the water-exposed surface (Fig. 7, 2nd curve) except that illumination causes the appearance of a small peak at 14.6 eV that is not visible in the $\Delta N$ dark spectrum.

Water exposure causes an increase in the work function of $0.7 \pm 0.1$ eV which is slightly reduced after illumination to $0.6 \pm 0.1$ eV. In the case of hydrogen exposure, $\Delta \phi = 0.9 \pm 0.1$ eV with reduction to $0.8 \pm 0.1$ eV after 100 minutes of illumination. When the clean reduced surface is u.v. illuminated, the change of the work function is within the experimental detection limit of 0.1 eV.

3.2. Stoichiometric SrTiO$_3$ crystal. High temperature annealed surface

In order to correlate the reactivity of the SrTiO$_3$(111) surfaces with the Ti$^{3+}$ surface concentration we performed several experiments on a stoichiometric (non $H_2$ reduced) crystal.

In the bottom curve of Fig. 8 we show the UPS spectrum corresponding to a stoichiometric SrTiO$_3$(111) annealed at high temperature ($\sim 700^\circ C$ for a few minutes) and subsequently cooled to room temperature. Since there is no visible (resolved) peak emerging from the background in the 1 eV region, this surface has no detectable
concentration of Ti$^{3+}$. The O (2p) bands appear clearly separated, showing emissions at 5.2 eV ($\pi$ symmetry) and at 7.5 eV ($\sigma$ symmetry). In the 12 eV region no peak is visible. A LEED pattern $p(1x1)$ consistent with the unreconstructed termination of the bulk was observed. This surface is chemically inert. $10^3$-$10^4$ Langmuirs of hydrogen or oxygen exposures did not induce any changes in the UPS spectrum. Band gap illumination for 17 hours did not produce any Ti$^{3+}$ emission. When the high temperature annealed surface of the stoichiometric crystal was Ar bombarded, the UPS spectrum show in the top curve of Fig. 8 was obtained. It shows a Ti$^{3+}$ emission with intensity about one half that seen from the reduced crystal under similar conditions. The 2p oxygen bands are almost unresolved and a peak at ~12 eV appears.

When the high temperature annealed surface was sputtered with hydrogen instead of argon the results shown in fig. 9 were obtained. In the top curve we show the UPS spectrum corresponding to the clean, high temperature annealed surface. Hydrogen sputtering at $2 \times 10^{-5}$ Torr of hydrogen and 500 eV accelerating voltage produced the changes shown in the second to fourth curves in Fig. 9. We observe that as a function of the sputtering time the O 2p part of the spectrum evolves in such a way that the initial splitting of the two oxygen emissions becomes weaker and is no longer resolved after 9 minutes of bombardment. The Ti$^{3+}$ emission (initially zero) does not increase as a consequence of the $H_2$ sputtering, in contrast to the results from Ar
sputtering. We also observe a small peak at 12 eV (shown with an arrow in Fig. 9) induced by the H$_2$ sputtering. When the surface sputtered with H$_2$ for 9 minutes is band gap illuminated for 17 hours, a very small, but non zero peak appears in the 1 eV region indicating a small photogeneration of Ti$^{3+}$. 
4. Discussion

H₂ or H₂O adsorption or band gap illumination produce surface hydroxyl groups on the clean reduced SrTiO₃(111) surface. In these cases the hydroxyl-induced UPS spectra show an emission located at 11.8 eV below the Fermi level (see Fig. 7). Even the "clean reduced surface appears to be partially hydroxylated since we also observe an emission at 12 eV in the UPS spectrum of the clean reduced surface (Fig. 1). This peak is not visible in the high temperature annealed stoichiometric crystal (Fig. 8, bottom curve) but it appears when this surface is Ar sputtered (Fig. 8, top curve) or H₂ sputtered (Fig. 9). It is well known from infra-red spectroscopic studies (8,17,18) that a TiO₂ powder becomes dehydroxylated when evacuated and heated at temperatures greater than ~400°C. By analogy we can believe that the high temperature (~700°C) annealed surface in the stoichiometric crystal will be fully dehydroxylated. Electron stimulated desorption studies (19) show a significant presence of surface hydroxyls in a Ar sputtered TiO₂ single crystal surface that has not been exposed to any gas (except of course to the background gases in the UHV system). It is therefore possible to conclude that the peak at ~12 eV is indicative of surface hydroxyls. The appearance of this peak indicates that even the "clean" reduced surface appears to be partially hydroxylated.

In order to produce surface hydroxyls, hydrogen in some form must be present at the surface. UPS studies of H₂ adsorption on pure Ti metal (20) show that hydrogen sticks very well on the pure Ti. In
fact, it is not possible to obtain clean Ti surfaces due to the adsorption of the background H\textsubscript{2} in the UHV system. This adsorption is dissociative, and results in a large change in the Ti d-band UPS intensity indicating that the surface Ti atoms bond H atoms via the Ti d electrons. Our data also suggest that the Ti d electrons are necessary to bind hydrogen to the SrTiO\textsubscript{3}(111) surfaces. In the high temperature annealed stoichiometric surface with no Ti\textsuperscript{3+} present we observe no hydrogen adsorption even after exposures of 10\textsuperscript{6} L of H\textsubscript{2}. Hydrogen must be implanted at high ion energies in order to introduce it on the surface. Ar bombardment of the high temperature annealed surface generates Ti\textsuperscript{3+} ions that are able to dissociate H\textsubscript{2} molecules allowing hydroxylation of the surface.

The surface reactivity upon oxygen adsorption is also related to the presence of Ti\textsuperscript{3+} species. The high temperature annealed surface in the stoichiometric crystal appears to be very inert to oxygen exposure whereas the clean reduced surface (Ti\textsuperscript{3+} rich) readily adsorbs oxygen. We can obtain a rough idea of the amount of adsorbed oxygen by examining the XPS spectra in Fig. 4 and by using the attenuation factor \(e^{-2dn/\lambda \cos \theta}\) as we discussed in Section 3.1.1. The intensity of the positive peak in curve c of Fig. 4 is 13\% of the intensity of the 0 peak in curve a. For a stoichiometric unreconstructed SrTiO\textsubscript{3}(111) crystal, the contribution of surface oxygen to the total O (1s) emission would be of 18\%, not very different from the above mentioned value. Thus oxygen adsorption and photodesorption on the clean reduced surface occurs in the range of about one monolayer.
As we have mentioned in Section 3.1.4, the three lower curves in Fig. 7 exhibit about the same peak intensities. Thus, the hydroxyl concentrations resulting from these experiments are similar. The work function changes, however, are different: +0.7 eV for water adsorption, +0.9 for H₂ and 0.1 for the irradiation without any gas exposure. These differences probably indicate that different hydroxyl species are formed in each case as indicated by the observations of Munuera et al. (17). By using infra-red spectroscopy, different hydroxyl species in TiO₂ powders were detected depending on the sample treatment. When hydrogen is adsorbed on the clean reduced SrTiO₃(111) surface, illumination regenerates Ti³⁺ ions. This regeneration does not occur if the surface has been exposed to water. This observation also indicates that the nature of hydroxylatoiion is not identical in these two cases.

There are several reports on SrTiO₃ and TiO₂ (8,17,18) which show that surface hydroxylation is a necessary condition for surface photoactivity. We have also obtained results to add to this body of data. Band gap irradiation of the dehydroxylated high temperature annealed surface (stoichiometric crystal) does not generate Ti³⁺, but if this surface is hydroxylated (by means of hydrogen sputtering), a very small but nonzero Ti³⁺ photogeneration is visible.
5. Conclusions

On the reduced, SrTiO$_3$(111) crystal surfaces,

a) Ti$^{3+}$ species is present on the surface region in amounts exceeding one monolayer.

b) The Ti$^{3+}$ concentration is reduced when the surface is exposed to H$_2$, H$_2$O or O$_2$. Subsequent band-gap irradiation partially restores the Ti$^{3+}$ initial concentration in the cases of H$_2$ and O$_2$ exposed surfaces, but not in the case of exposure to H$_2$O. XPS and UPS data show that the Ti$^{3+}$ photogeneration on the surface exposed to oxygen is accompanied by a decrease in the surface oxygen content, indicating that oxygen photodesorption is taking place.

c) UPS data show that hydroxyl species are present on the "clean" surface. The surface hydroxyl concentration increases when water or H$_2$ are introduced into the vacuum system or when the surface is irradiated with band gap light.

On the stoichiometric high temperature annealed SrTiO$_3$(111) crystal surfaces, there is no Ti$^{3+}$ present. This surfaces are chemically very inert. H$_2$ sputtering causes surface hydroxilation.
Acknowledgements

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15. The possibility of non dissociative water adsorption was also
    considered. Attempts to align the water induced UPS peaks at 4.6,
    6.5 and 11.8 eV with the peaks due to gas phase molecular water,
    lead to an important mismatch indicating that non dissociative
    water adsorption does not occur.
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Figure Captions

Fig. 1. AES, XPS Ti(2p) and O(1s) and UPS spectra of the reduced SrTiO$_3$(111) crystal after Ar sputtering and moderate annealing.

Fig. 2. Ti(2p) XPS spectra of (a) the clean reduced surface, (b) the same after 0.5 L of oxygen exposure. Curve (c) shows the difference spectrum due to the oxygen adsorption.

Fig. 3. Left: Evolution of the concentration of Ti$^{3+}$ when O$_2$, H$_2$ and H$_2$O are adsorbed in the dark, as a function of the gas exposure.

Right: Effect of subsequent band gap illumination on the Ti$^{3+}$ concentration as a function of irradiation time.

Fig. 4. (a) O(1s) XPS spectrum of the clean reduced surface, (b) after 100 L of oxygen exposure. (c) Difference spectrum due to the oxygen adsorption. (d) Difference spectrum after 100 minutes of band gap illumination of the oxygen exposed surface.

Fig. 5. UPS difference spectra due to an exposure of 2 x 10$^3$ L of oxygen on the clean reduced surface (upper curve), and to the subsequent band gap illumination (lower curve).

Fig. 6. UPS spectra of a NaOH pellet (upper curve) and of a film of NaOH on the SrTiO$_3$ crystal (lower curve).
Fig. 7. Upper curve, UPS spectrum of a film of NaOH on the SrTiO$_3$ crystal. 2nd, 3rd and 4th curves, UPS difference spectra due to $2 \times 10^3$ L water exposure in the dark, $2 \times 10^3$ L hydrogen exposure in the dark and 110 minutes of band gap irradiation on the clean reduced surface.

Fig. 8. Lower curve, UPS spectrum of the stoichiometric crystal after annealing at high temperature.

Upper curve: UPS spectrum after Ar bombardment of the high temperature annealed surface of the stoichiometric crystal.

Fig. 9. Evolution of the UPS spectrum of the high temperature annealed stoichiometric crystal as a function of the hydrogen sputtering time.
Fig. 1
Fig. 2

XPS, Ti (2p)
reduced SrTiO$_3$(III)

N(E) (a.u.)

a) Initial, clean surface

b) = a) + 0.5 L O$_2$

c) = b) - a)

ΔN(E) (a.u.)

Binding energy (eV)
Fig. 3
XPS, O(1s) reduced SrTiO₃(III)

N(E)
(a.u.)

X₂

8N(E)
(a.u.)

ΔN(E)
(a.u.)

Binding Energy (eV)

a) Initial, clean surface, dark

b) = a) + 100 L. O₂

c) = b) - a)

d) = b) + 100 min U.V. illumination - a)

XBL799-7049

Fig. 4
Fig. 5

UPS, $\Delta N(E)$
reduced SrTiO$_3$(III)

$\Delta N(E)$ (a.u.)

Binding energy (eV)

11.4
4.5
5.8

$2 \times 10^3$ L O$_2$

$2 \times 10^3$ L O$_2^+$

40 min. irrad.

0 = $E_F$

XBL 799-7044
Fig. 6
Fig. 7

UPS reduced SrTiO$_3$ (III)

N(E):

~1 micron thick NaOH Film on reduced SrTiO$_3$ (III)

$N(E)$:

$\Delta N(E)$:

$2 \times 10^3$ L H$_2$O

$2 \times 10^3$ L H$_2$

110 min.

U.V. irradiation

$O = E_F$

Binding energy (eV)
Fig. 8

UPS
stoichiometric
SrTiO$_3$(III)

Ar Sputtered

High Temp. Annealed

$N(E)$
(a.u.)

Binding energy (eV)

0 = $E_F$

12.0
6.5
5.6
7.5
5.2
0.8

XBL799-7043
UPS $N(E)$
stoichiometric
SrTiO$_3$(III)

$N(E)$
(a.u.)

High Temp.
Annealed

After 2 min.
Hydrogen
Sputtering

" 4 min.

" 9 min.

Binding energy (eV)

$0 = E_F$

XBL799-7041

Fig. 9