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Y. W. Chung, W. J. Lo, and G. A. Somorjai

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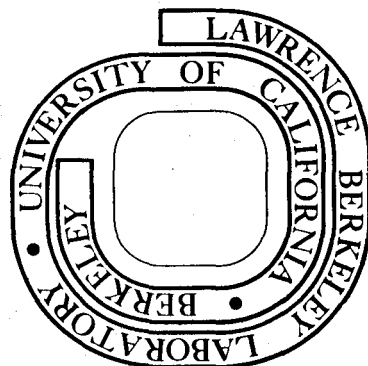
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LOW ENERGY ELECTRON DIFFRACTION AND ELECTRON SPECTROSCOPY
STUDIES OF THE CLEAN (110) AND (100) TITANIUM DIOXIDE (RUTILE) CRYSTAL
SURFACES

by

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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(510 eV)/Ti(380 eV) 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 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

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bulk valence band maximum to the Fermi level. High energy electron beams (1.6 keV 20 μ A) 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 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 ~ 0.5 volt to the titanium dioxide electrode. Without an applied potential the surface band-bending on the TiO₂ 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 ≥ 0.5 volt on the TiO₂ 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. The structure and electronic properties of

Except for the work of Henrich et al⁽⁹⁾, 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 1×10^{-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 analyser (CMA) with a coaxial electron gun was used as the primary electron source and electron energy analyser. In all AES analyses, the CMA was operated at a constant resolution of 1.5 eV. In this way, we could resolve detailed structures/in the Auger spectra and give reliable estimates⁽¹⁰⁾ of the oxygen-to-titanium ratios under different conditions of surface preparation

In obtaining the electron energy loss spectra, the analyser was operated in the retard mode with pass energy set at 50 eV. However since the primary electron beam was not energy analysed, 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 $-\frac{d^2N}{dE^2}$ 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 ~ 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 He I 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 coincident 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 analyser was operated with a constant resolution of 0.35 eV. Typically a spectrum could be obtained in 5-10 minutes.

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 1.0μ

Al_2O_3 powders. Gross contaminants on the surface were then removed by etching the specimen in 50°C 5N NaOH solution for 30 minutes. 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 $8 \mu\text{A}$ (resp. $1 \mu\text{A}$) to the sample surface.

3. SELECTED PROPERTIES OF TITANIUM DIOXIDE (RUTILE)

Titanium dioxide can exist in 3 crystallographic forms, viz. anatase, brookite and rutile. The rutile structure is tetragonal⁽¹¹⁾, with $a=b=4.59 \text{ \AA}$ and $c=2.96 \text{ \AA}$ (Fig. 1). Physical properties such as electrical conductivity and dielectric constant are highly anisotropic.

TiO_2 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⁽¹²⁾. The optical band gap is 3.0 eV near room temperature⁽¹¹⁾. The pure undoped crystal is thus transparent with a

yellowish tint.

The phase diagram⁽¹³⁾ of the O-Ti system is complicated. Below $\sim 1830^\circ\text{C}$ (m.p. of TiO_2), there exist at least eight intermediate titanium oxides ($\text{Ti}_n\text{O}_{2n-1}$, $n=3$ to 10) between Ti_2O_3 and TiO_2 . On reduction by heating in vacuum or hydrogen at 600°C for an hour, oxygen is partially lost from the TiO_2 lattice (equilibrium oxygen partial pressure above TiO_2 at 600°C being about 10^{-18} torr⁽¹⁹⁾) and the crystal becomes blue in color. In this circumstance, transport measurements indicate that the crystal becomes N-type and paramagnetic resonance study shows the presence of Ti^{3+} species⁽¹¹⁾. The oxygen concentration can be restored by heating the reduced crystal in an oxygen atmosphere (~ 200 torr) at 600°C for 1 hour, as shown by the color change of the crystal from blue to yellow.

4. RESULTS

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 $\geq 10^3$ seconds before annealing. The Auger electron spectra for clean argon ion-bombarded and annealed (at 600°C) TiO_2 (110) surfaces are shown in Fig. 2. Note the increase in the O(510 eV)/Ti(380 eV) ratio from ~ 1.3 on the argon ion bombarded surface to ~ 1.7 on the annealed TiO_2 (110) surface. This ratio is fairly reproducible over many sputtering-annealing cycles on different crystal faces of TiO_2 . On the other hand, on bombarding a clean and well ordered TiO_2 (110) surface at room temperature

with $\sim 7.2 \times 10^{15}$ oxygen ions/cm², the O(510)/Ti(380) ratio remains essentially unchanged, viz. ~ 1.7 .

LEED showed that the (110) surface has a stable (1x1) 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 (1x3) surface structure. Further annealing up to 800°C gave rise to a (1x5) structure. A surface with a (1x7) structure was obtained when the crystal was heated at $\sim 1200^\circ\text{C}$ 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. 2(b), there is a large variation in the O(510 eV)/Ti(380 eV) ratio, decreasing from ~ 1.7 for the (1x3) surface to ~ 1.3 for the (1x7) 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 in the LEED pattern or the Auger spectrum. However, a 2-minute exposure to a 1.6 kv, 20 μA 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)-(1x3) surface was exposed briefly (30 minutes 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.

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 (1x3) surface structure, marked changes show up in the energy loss spectrum, viz. the appearance of a loss peak at 3.2 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)-(1x3) surface. On the (100)-(1x5) surface, the energy loss spectrum shows the reappearance of the 1.6 eV transition (Fig. 6c). The (1x7) surface has a loss spectrum similar to that of the (1x5) 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 (1x3) surface, transitions at 8.2, 5.2 and 2.4 eV are all surface sensitive, whereas transitions at 13.5, 10.1 and 5.8 eV are due to bulk TiO_2 interband excitations⁽⁹⁾.

High energy electron beams were found to have a significant effect on the energy loss spectra of TiO_2 surfaces. Fig. 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 seconds. The latter spectrum resembles closely to that from an argon ion sputtered surface.

3. Ultraviolet Photoemission Spectroscopy

The UPS spectra for different TiO_2 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 TiO_2 (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 TiO_2 (110) surface (Fig. 9). Annealing at 600°C resulted in the weakening of these two peaks, together with marked changes in the valence band emission, as shown in Fig. 8(b).

The valence band structure of the TiO_2 (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) resembles closely to 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 (=hv-width of photoelectron energy distribution) increased from 4.6 eV for the TiO_2 (110) argon bombarded surface to 5.5 eV for the well annealed (110) 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 7.2×10^{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 ± 0.2 eV for both the annealed or^{oxygen} ion bombarded (110) and (100)-(1x3) surfaces and 0.9 ± 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 annealing the sputtered surface, oxygen diffuses from the bulk to the surface, thereby increasing the oxygen concentration on the surface. The decrease in the surface oxygen concentration during annealing at temperatures higher than 800°C is due to the removal of oxygen from the surface. Therefore, at any temperature, the surface oxygen concentration is determined by two competing processes, viz. the diffusion of oxygen from the bulk to the surface and the escape of oxygen from the surface. After using the crystal for many sputtering-annealing cycles, the O(510 eV)/Ti(380 eV) ratio on the surface drops to below the normal value of ~ 1.7 on the (100)-(1x3) 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 TiO_2 surface as a result of argon

sputtering, the energy loss spectrum of the argon ion sputtered TiO_2 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 Ti^{3+} interband transition. The same 1.6 eV ELS transition was also found on TiO_2 surfaces disordered by oxygen ion or high energy electron beam bombardment, in which the surface oxygen concentration remained unchanged, as well as in the TiO_2 (100)-(1x5) and (1x7) surfaces, in which a decrease of the surface oxygen concentration occurred. Therefore, it appears that surface Ti^{3+} species are formed as a result of either the displacement of 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 TiO_2 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.

Since the band gap of TiO_2 is 3 eV, the initial state for the ELS transition at 2.4 eV on ordered TiO_2 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 TiO_2 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 1.6 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 TiO₂ (110) surface.

The UPS spectra from TiO₂ 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 TiO₂ valence bands. However, to date, there are no surface band structure calculations made for the TiO₂ 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^(6,17). The UPS spectra so obtained compare very closely with those from TiO₂ 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 TiO₂ surfaces in our work (Fig. 9). This confirms Eastman's suggestion⁽¹⁷⁾ that a (disordered) TiO₂ 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 TiO₂ 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 7.2×10^{15} ions/cm² causes no observable changes. From AES and UPS studies, one finds that the work function and surface band bending of clean TiO₂ 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 Ti⁴⁺ to give Ti³⁺ (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 TiO₂ (110) surface and the same surface bombarded with argon ions, on exposure to the ambient atmosphere.

In photo-induced reactions where the transport of photogenerated charge carriers at the surface (e.g. transport of holes to the TiO₂ 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 the/semiconductor surface. The ability to change the work function and surface band-bending by different surface treatments such as argon ion bombardment and annealing, as demonstrated 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 to study and characterize single crystal surfaces of titanium dioxide (rutile). LEED showed that both the (110) and (100) surfaces are stable, with the latter surface giving rise to three distinct surface structures, viz. (1x3), (1x5) and (1x7) 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)-(1x3), (1x5) and (1x7) surface structures correlates with the decrease in the $\text{O}(510 \text{ eV})/\text{Ti}(380 \text{ eV})$ ratio from ~ 1.7 to ~ 1.3 , as shown by AES.

The (110) and (100)-(1x3) 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)-(1x5) and (1x7) 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

TiO₂ 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 TiO₂ surface with recent work on oxygen adsorption on titanium film surface^(16,17) suggests that a disordered TiO₂ layer is formed by exposing a freshly evaporated titanium film to ~100L oxygen at room temperature.

Low-energy (50-200 eV) electron irradiation does not have any observable effects on the surface composition, structure and electron state distribution of clean TiO₂ surfaces. However, initially clean and well-ordered TiO₂ surfaces are disordered by electron beams normally used in Auger analysis (1.6 kv, 20 μ A), as demonstrated by LEED, energy loss and ultraviolet photoemission spectroscopies from these surfaces. The work function and band-bending of clean ordered TiO₂ (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.

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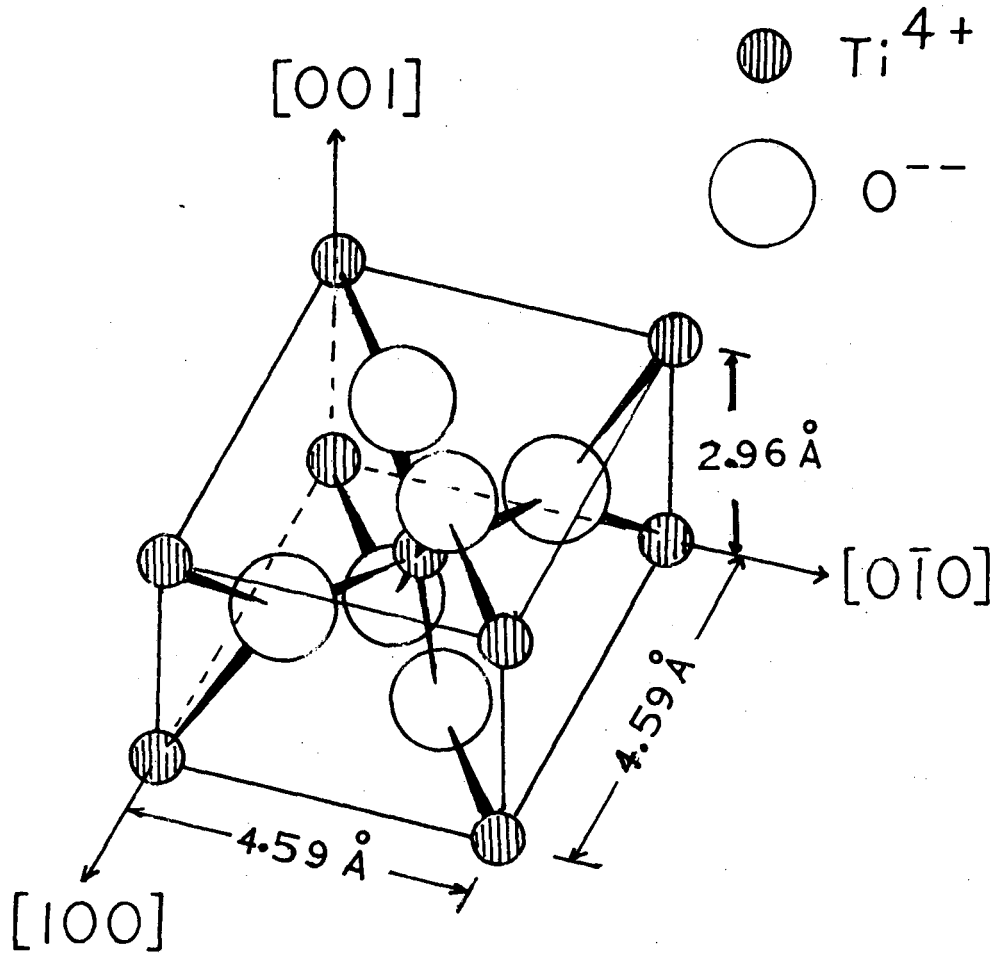
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14. Surface band-bending $= E_{c,s} - E_{c,b} = (E_{c,s} - E_F) + (E_F - E_{c,b})$ where $E_{c,s}$ and $E_{c,b}$ are the energy positions of surface and bulk conduction band minimum respectively. The first term is equal to (work function-electron affinity) 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.

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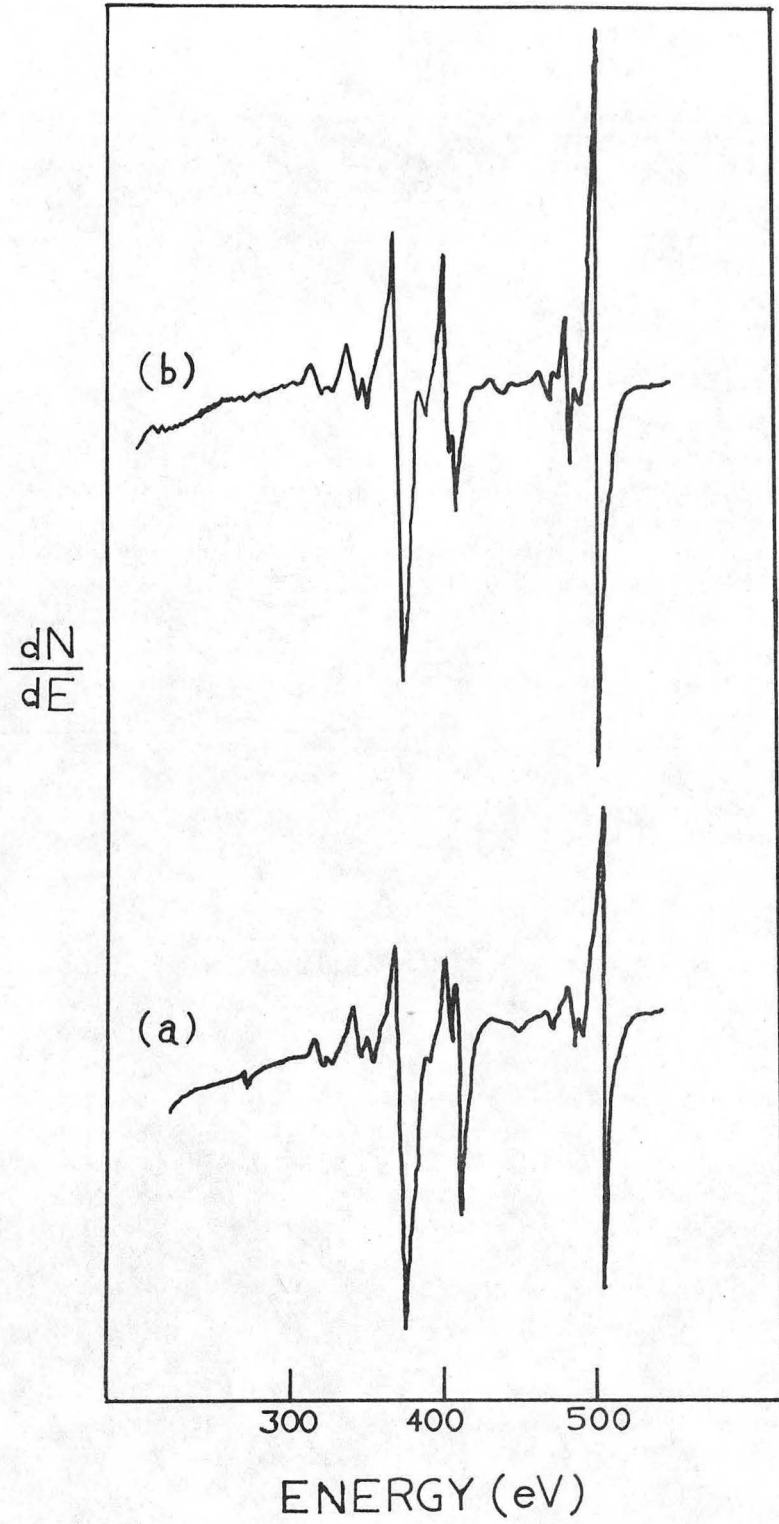
Figure Captions

1. The titanium dioxide (rutile) crystal lattice.
2. Auger electron spectra of (a) argon ion bombarded and (b) annealed TiO_2 (110) surface.
3. LEED pattern from a clean ordered TiO_2 (110) surface at an electron incident energy of 92 eV.
4. LEED patterns from clean TiO_2 (100)-(1x3), (1x5) and (1x7) surfaces. The primary electron energies are 110, 62 and 60 eV respectively.
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.
6. Electron energy loss spectra of (a) argon ion bombarded TiO_2 (100), (b) TiO_2 (100)-(1x3) and (c) TiO_2 (100)-(1x5) surfaces. Transitions labelled with (*) are surface-sensitive.
7. Effect of electron beam irradiation on the TiO_2 (110) surface. The dotted curve is the loss spectrum from a freshly annealed TiO_2 (110) surface and the solid curve is the spectrum from the same surface after being irradiated by 1.6 kV 20 μ A electron beams for 100 seconds.
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.
9. UV photoemission spectrum from an initially clean and well-ordered TiO_2 (110) surface irradiated by 7.2×10^{15} ions/cm², obtained with $h\nu = 21.2$ eV at a resolution of 0.35 eV.



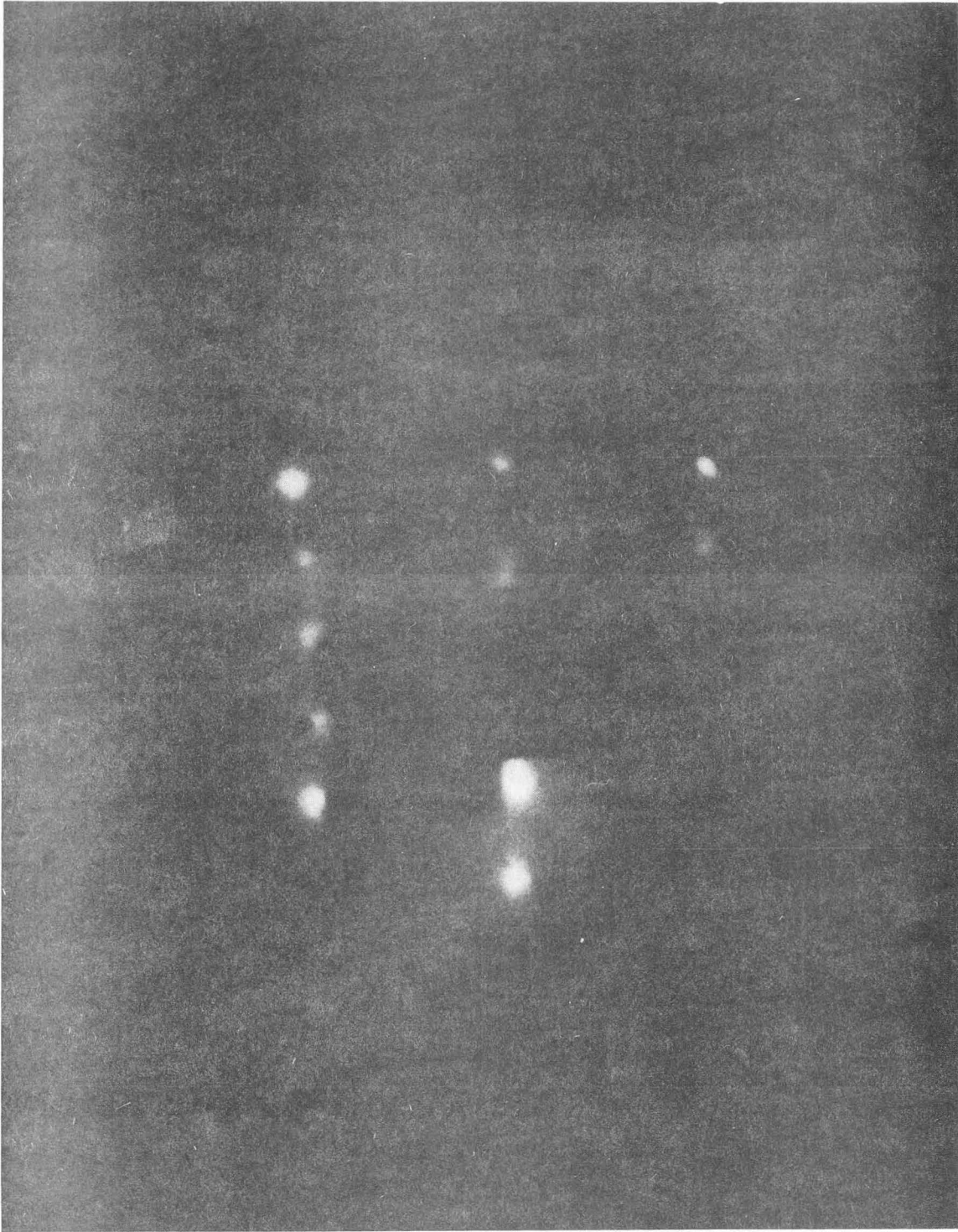
XBL769-10513

Fig. 1



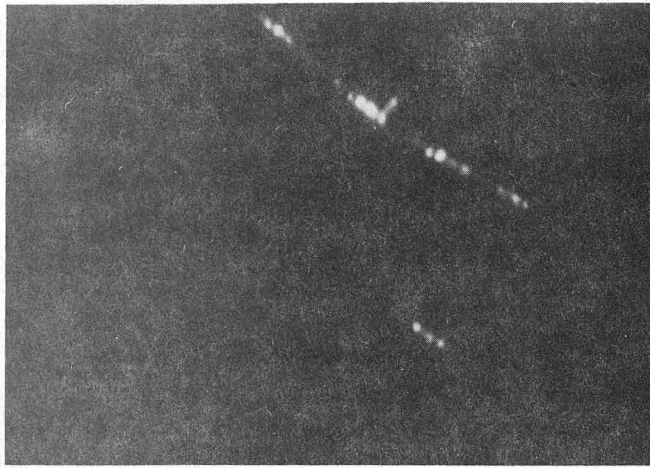
XBL 769-10402

Fig. 2

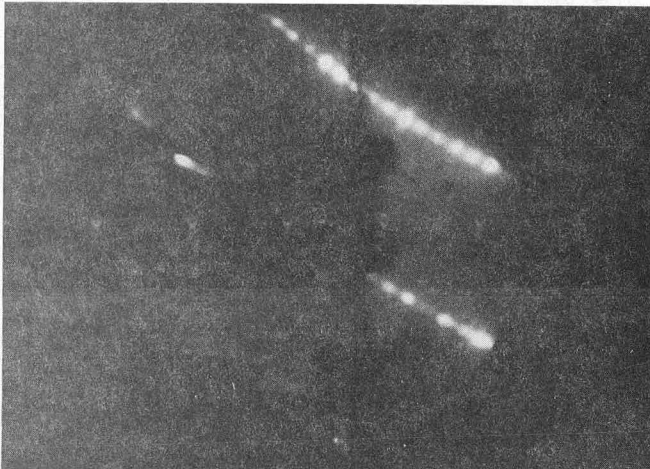


XBB 769-8154

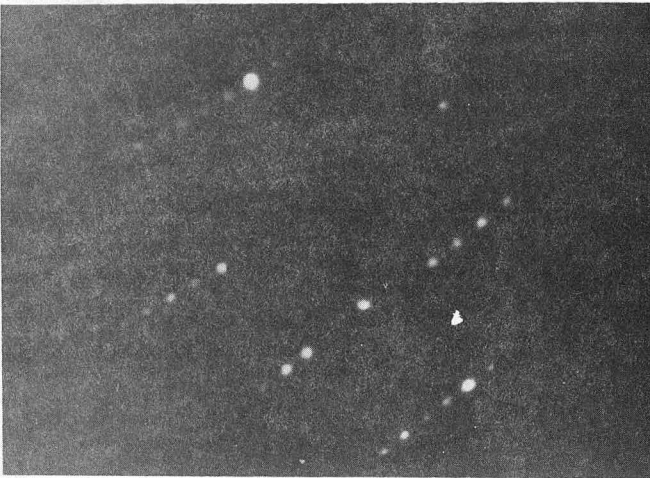
Fig. 3



(14x1)



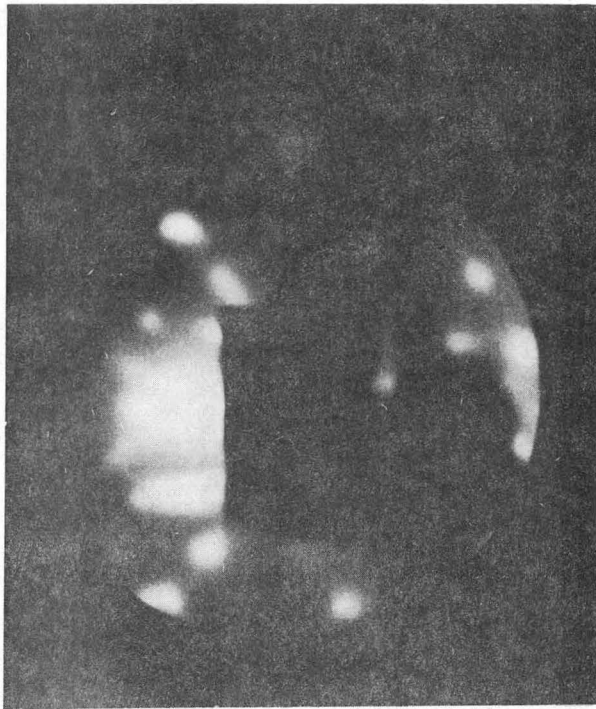
(10x1)



(6x1)

XBB 769-8153

Fig. 4



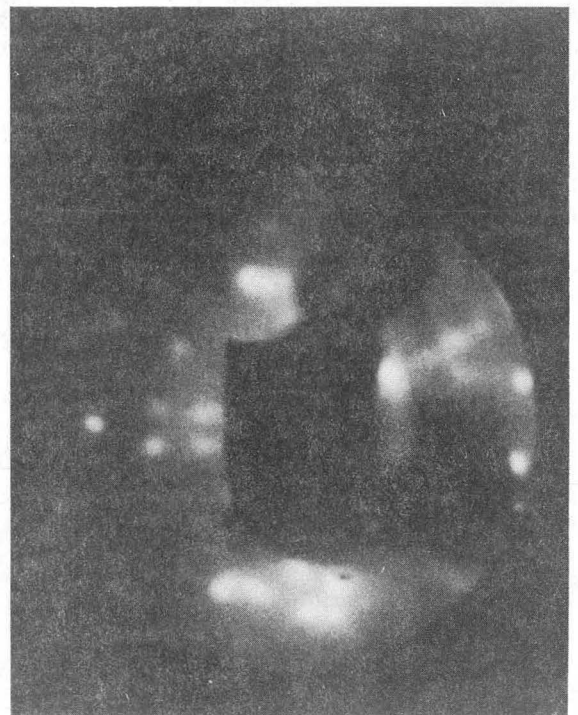
25 eV



27 eV



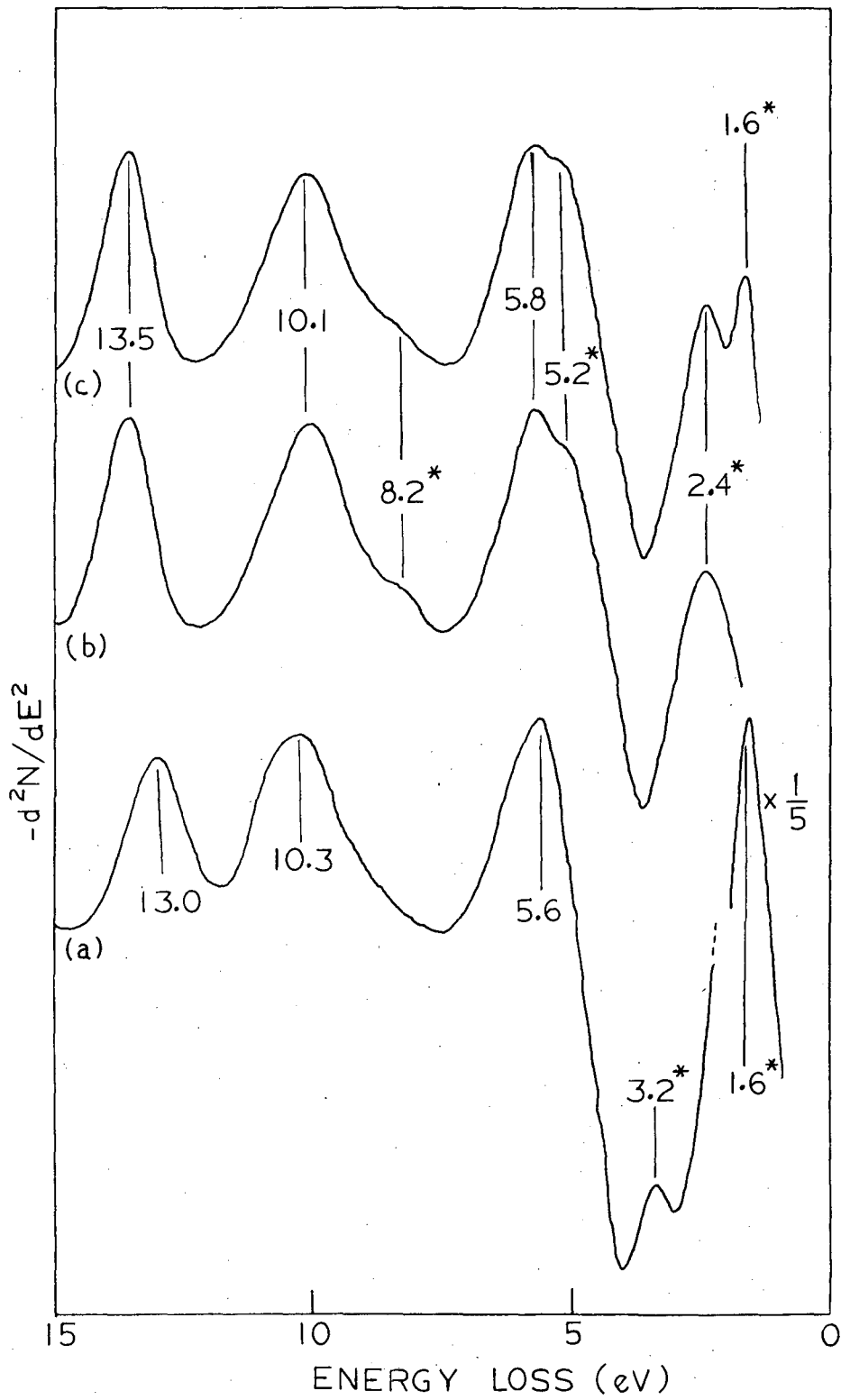
29 eV



33 eV

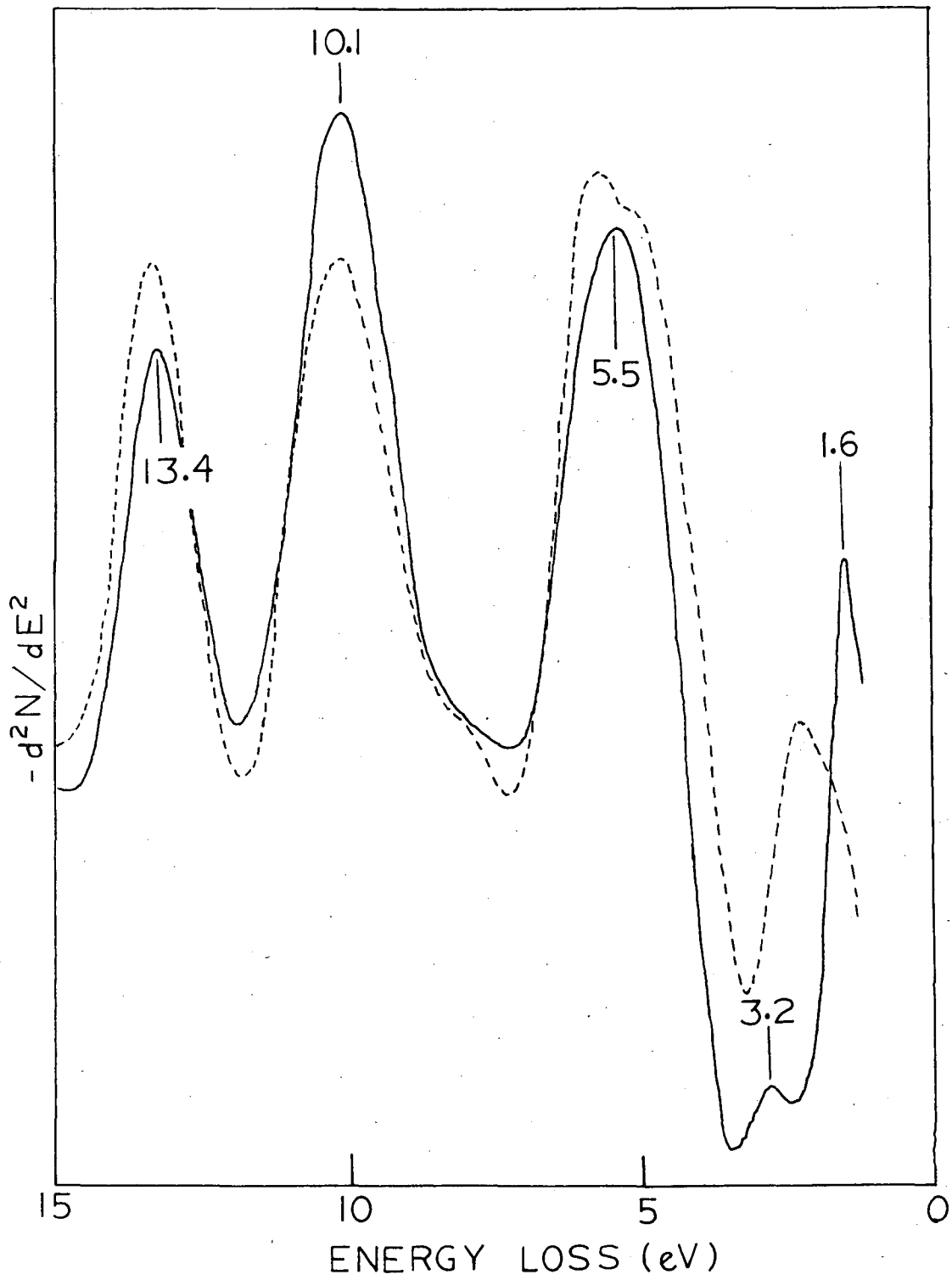
Fig. 5

XBB 766-5835



XBL 769-10404

Fig. 6



XBL 769 10403

Fig. 7

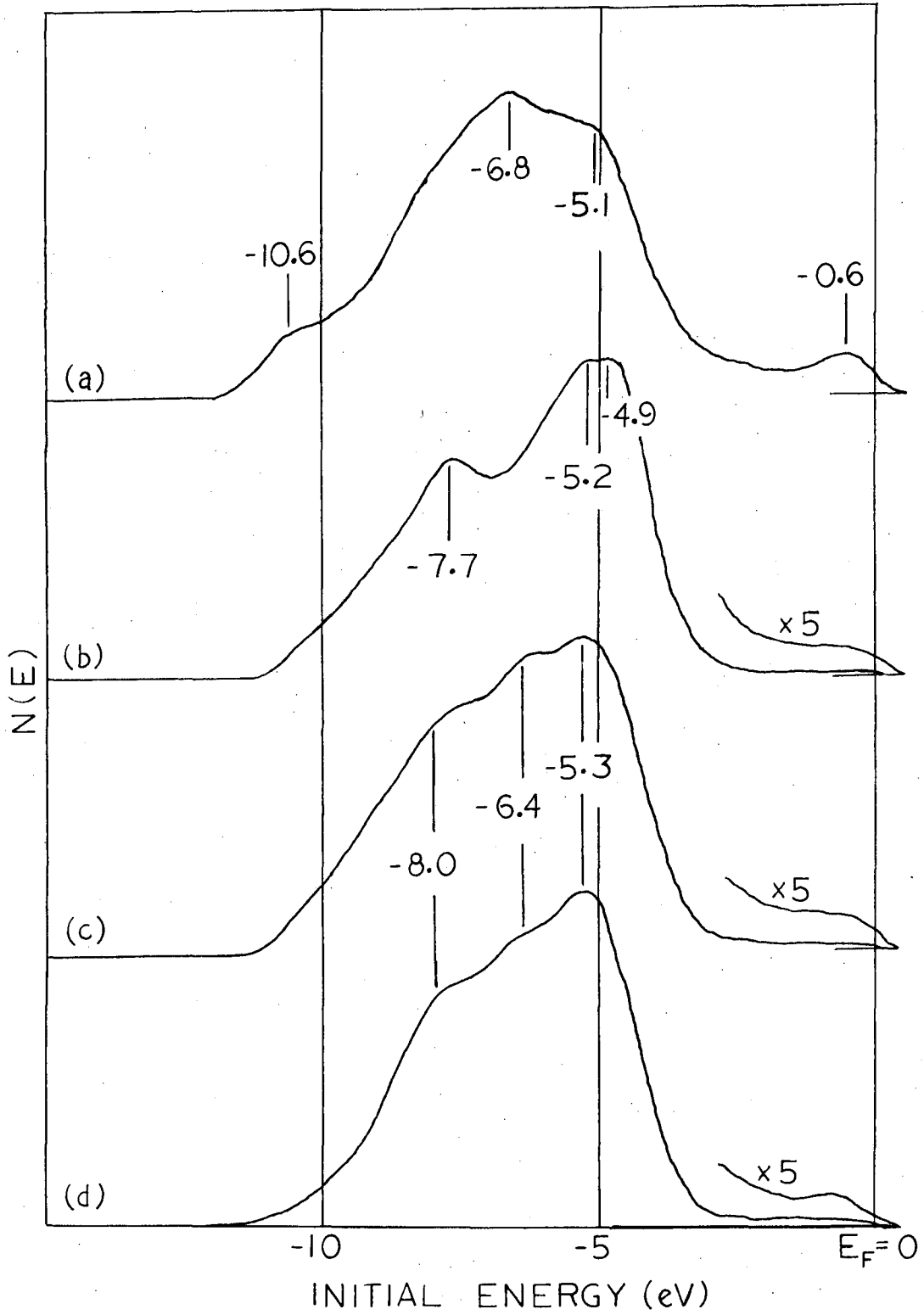
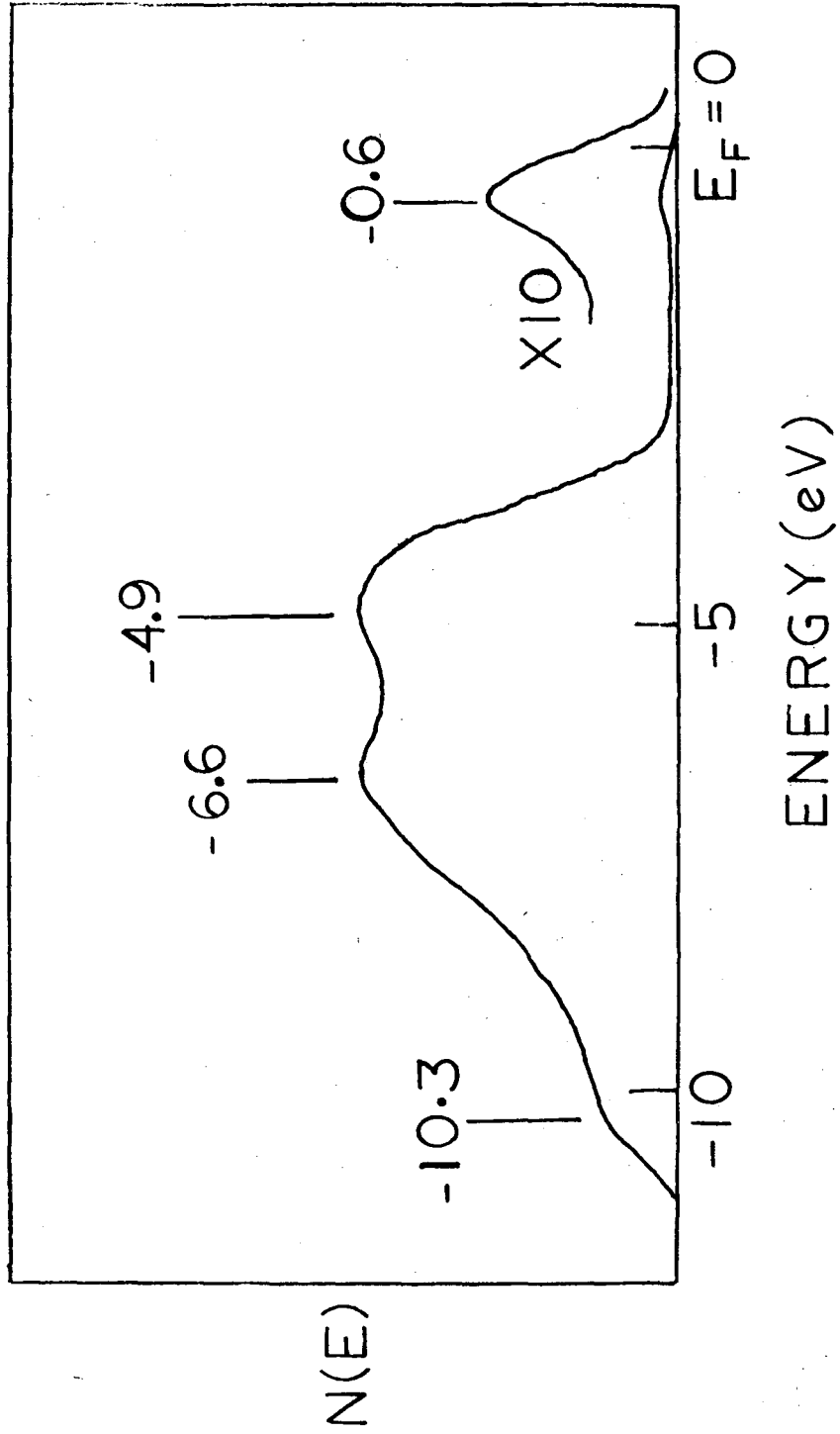


Fig. 8



XBL769-10514

Fig. 9

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