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Surface spectroscopy studies of the $SrTiO_3$ (100) surface and the platinum-$SrTiO_3$ (100) interface

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Auger-electron spectroscopy (AES), low-energy-electron diffraction (LEED), electron-energy-loss spectroscopy (ELS), and ultraviolet-photoelectron spectroscopy (UPS) were used to characterize the composition, structure, and electronic properties of the strontium-titanate (100) surface and the platinum–strontium-titanate interface. The strontium 65-eV Auger signal on the clean strontium-titanate surface decreases abruptly as the temperature is raised beyond 240 °C. Partial ordering occurs when platinum is deposited on the strontium-titanate (100) surface as evidenced by LEED. Platinum appears to remove surface Ti^{3+} by electron transfer from $SrTiO_3$ to platinum. These results are discussed in light of the findings in photoelectrolysis and other photocatalytic studies using $SrTiO_3$.

I. INTRODUCTION

Several interesting studies were made recently on the surface properties of strontuim titanate. Lo and Somorjai found that the surface concentration of strontium on the $SrTiO_3$ (111) 1×1 surface as determined by Auger-electron spectroscopy decreases with increasing temperature in a reversible manner.[1] In addition, when the $SrTiO_3$ (111) 1×1 surface is produced by room-temperature argon-ion sputtering and subsequent annealing at 600 °C, a signficant concentration of Ti^{3+} is always present on the surface, as reflected in the existence of an energy-loss transition at 1.6 eV and band-gap emission in the ultraviolet-photoelectron spectroscopy (UPS) spectrum.[1] Similar band-gap emissions were observed earlier by Powell and Spicer[2] on a cleaved $SrTiO_3$ (100) surface which was previously reduced by heating in hydrogen. Henrich *et al.* noted that these band-gap states can be depopulated by exposure to oxygen.[3] Also, there is no appreciable band bending on the clean (100) surface, independent of whether the surface is prepared by vacuum fracture or annealing after ion bombardment.[4] This is consistent with the conclusion that the band-gap Ti^{3+} *d* electrons are provided by oxygen vacancies, not by the $SrTiO_3$ bulk.[4,5]

Work has also been done on the surface composition of titanium dioxide and strontium titanate before and after they are subjected to extended high-current photoelectrolysis.[6] These studies showed that prolonged photoelectrolysis results in the decrease of Ti^{3+} species and increase of oxygen concentration on the semiconducting electrode surface.[6] Other electrochemical studies indicated that this leads to loss of photoelectrolysis activity and even corrosion.[7] This strongly suggests the importance of surface Ti^{3+} in photoelectrolysis.[1,5,8]

Wrighton *et al.* demonstrated recently that by plating a thin platinum layer onto a strontium-titanate electrode and then illuminating the semiconductor with band-gap radiation in an aqueous electrolyte, hydrogen and oxygen were found to evolve from the platinum and strontium-titanate surface, respectively.[9] This may be contrasted with a standard two-electrode electrochemical cell configuration.[10] Wrighton *et al.* also found that the efficiency degrades after several hours of photoelectrolysis.[9]

The photocatalytic activity of $SrTiO_3$ was also studied in the gas phase in the decomposition of water vapor into hydrogen and oxygen[11] and in the reaction of H_2O and CO_2 to give methane.[12] The latter work seems to indicate that a platinum contact on the $SrTiO_3$ surface is necessary for the reaction to occur.

In this paper, we report studies of the surface electronic properties of the $SrTiO_3$ (100) surface and the Pt-$SrTiO_3$ (100) interface. We find that the strontium surface concentration changes abruptly at about 240 °C while titanium and oxygen surface concentration remain constant as a function of temperature. By evaporating a controlled amount of Pt onto the $SrTiO_3$ (100) surface, we find that there is an electron transport from the $SrTiO_3$ to the platinum surface, resulting in the formation of a Schottky barrier. This result is discussed in light of the findings in photoelectrolysis and other gas-phase work using composite Pt-$SrTiO_3$ electrodes.

II. EXPERIMENTAL PROCEDURE

Studies were performed in a Physical Electronics model-548 UPS-Auger ultrahigh-vacuum chamber with a base pressure in the 10^{-10}-Torr range. The system is equipped with a cylindrical mirror analyzer (CMA) with a coaxial electron gun, an ion gun, a differentially pumped cold-cathode He discharge lamp, and low-energy-electron diffraction (LEED) optics.

First-derivative Auger spectra were obtained in the normal (nonretarded) mode at a beam voltage of 2 kV with a peak-to-peak modulation of 4 V. Energy-loss spectra were obtained in the retarded mode using pulse counting at a beam voltage ~ 100 V to give an overall energy resolution of 0.8 eV.

In UPS studies, the He lamp was operated at a pressure of 0.5 Torr to generate the He I line at 21.2 eV. The pressure inside the vacuum system usually rose to the mid-10^{-9}-Torr range when the valve between the vacuum system and the uv source differential pumping manifold was opened. This pressure rise was due to the influx of helium, as indicated by the mass spectrometer. The specimen was positioned with its surface normal coincident with the CMA axis. The angle of incidence of the uv photons was 70° from the normal. The spectra were obtained at a constant resolution of 0.3 eV.

The specimen used was a 99.99% undoped strontium-titanate single crystal from NL Industries. Flat slices of the crystal with (100) orientation were obtained using standard Laue back reflection techniques. They were polished using 1-μm Al_2O_3 powders and were checked to ensure that they were within 1° of the (100) orientation at the end of the polish. The samples were then mounted on a ceramic holder with a Chromel-Alumel thermocouple affixed to the crystal surface. The crystal was heated radiatively by a tungsten filament mounted behind the crystal. All crystals used in this experiment were reduced by heating in vacuum to give sufficient conductivity. Specimens were sputter cleaned using a 2-kV–20-μA argon-ion beam for a few minutes. Subsequent annealing at 450 °C for 40 min was sufficient to generate a clean ordered $SrTiO_3$ (100) 1×1 surface, as judged by Auger and LEED, respectively.

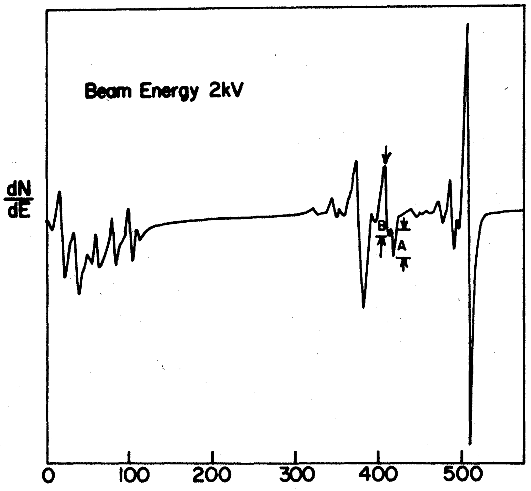

FIG. 1. Auger-electron spectrum of a clean $SrTiO_3$ (100) 1×1 surface obtained by room-temperature argon-ion sputtering and subsequent annealing at 450 °C.

Platinum deposition was accomplished using a home-built resistive heater made of multistrand tungsten wire coils onto which 2-cm lengths of Marz-grade platinum wires (from Materials Research Corporation) were attached. The platinum vapor beam was aimed at the focal point of the CMA where the specimen was located. The evaporation rate was $\lesssim 0.5$ Å/min and all evaporations were made with the specimen at room temperature. The platinum overlayer thickness was estimated from the growth of the platinum Auger peak at 64 eV and the attenuation of the oxygen Auger peak at 510 eV. It is important to outgas the whole evaporator thoroughly prior to deposition to minimize contamination of the $SrTiO_3$ surface during Pt evaporation.

III. RESULTS

A. Auger studies and LEED observation of the $SrTiO_3$ (100) 1×1 surface

The Auger spectrum of a clean ordered $SrTiO_3$ (100) 1×1 surface is shown in Fig. 1. The titanium

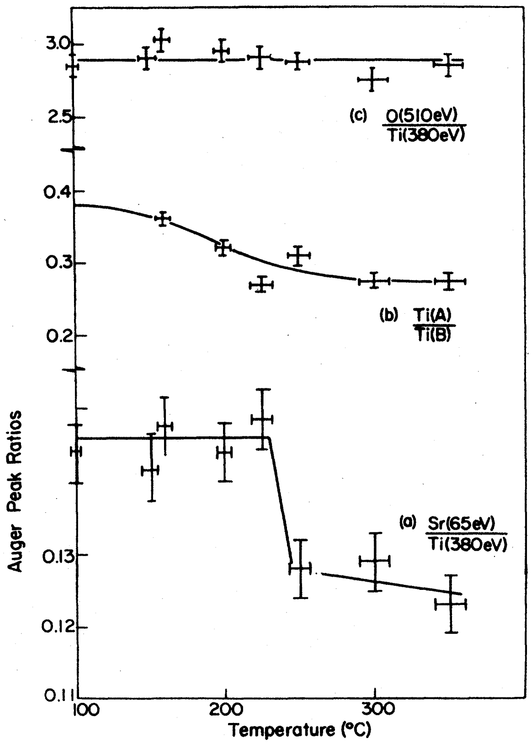

FIG. 2. Temperature dependence of various Auger-peak ratios. Data were taken in the first-derivative mode at a modulation voltage of 4 V peak to peak: (a) Sr(65 eV) to Ti(380 eV) ratio, (b) Ti(*A*) to Ti(*B*) ratio, and (c) O(510 eV) to Ti(380 eV) ratio.

Auger peaks around 410 eV show the usual doublet feature (*A* and *B* peaks) as reported previously.[1,4] The background between 0 and 100 eV is small because of our choice of the normal (nonretarded) mode operation. This facilitates accurate Auger-peak amplitude measurements in this energy range. The temperature dependence of the Sr(65 eV) to Ti(380 eV), O(510 eV) to Ti(380 eV), and Ti(*A*) to Ti(*B*) Auger-peak ratios are shown in Fig. 2. In measuring these Auger-peak ratios, care was taken to eliminate extraneous magnetic fields due to the crystal heater by turning off the heater current during measurements. The Sr(65 eV) to Ti(380 eV) Auger-peak ratio appears to drop abruptly as the temperature is raised from 225 to 250 °C. The O(510 eV) to Ti(380 eV) Auger-peak ratio stays relatively constant while there is a steady monotonic decrease in the *A* to *B* peak ratio in the temperature range of 100 to 350 °C. All these changes as a function of temperature are reversible.

The LEED pattern was observed in the temperature range of 100–225 °C and 250–400 °C. Except for the higher background expected of higher crystal temperatures, the strontium-titanate (100) surface gave the same (1 × 1) surface unit cell in both temperature ranges.

B. Platinum deposition on the $SrTiO_3$ (100) 1 × 1 surface

1. Auger and LEED studies

Figure 3 shows the evolution of the Auger spectrum in the energy range of 0 to 150 eV and 300–450 eV. At approximately $\frac{1}{4}$ monolayer (one monolayer is assumed to be 2.5 Å) platinum coverage, the strontium Auger peak at 65 eV is clearly attenuated. The rate of attenuation of the Sr(65 eV) peak with increasing Pt coverage appears to be larger than that of the Sr(86 eV) and Sr(105 eV) peaks, probably as a result of the shorter mean free path of 65-eV electrons in platinum. Further platinum deposition results in the growth of platinum Auger peaks at 42 and 63 eV. Small shifts (1 to 2 eV) in the Pt Auger-peak energies were observed as the average platinum coverage θ was increased from one to three monolayers.

While the strontium Auger peaks are simply attenuated with increasing Pt thickness, the titanium Auger-peak shape around 410 eV shows definite changes. In particular, the ratio of *A* to *B* (see Fig. 1) decreases with Pt coverage up to a monolayer. Beyond one Pt monolayer, the *A* to *B* ratio appears to increase.

Up to $\theta = 1$ we still observed a distinct 1 × 1 LEED pattern with a slight increase in background. Further increase in Pt coverage resulted in a diffused diffraction spot pattern, indicating the loss of long-range order on the surface.

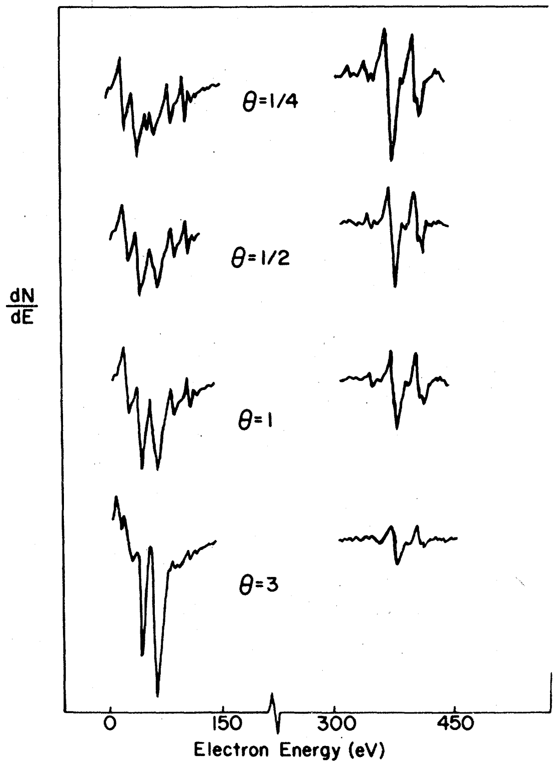

FIG. 3. Auger-electron spectra of the $SrTiO_3(100)$ surface with different coverages of platinum in the energy range of 0–150 eV and 300–450 eV. θ is the average Pt coverage in monolayers. One monolayer is assumed to be 2.5 Å.

2. Energy-loss spectroscopy studies

Figure 4 shows the energy-loss spectra obtained from the $SrTiO_3$ (100) surface with various coverages of platinum. The clean $SrTiO_3$ (100) 1 × 1 surface shows distinct loss peaks at 1.2, 6.0, and 13.0 eV,[13] in agreement with the results of Henrich *et al.*[4] on an ordered but nonstoichiometric $SrTiO_3$ (100) surface after sputtering and annealing. The most notable change with increasing platinum thickness is the rapid attenuation of the 1.2-eV transition (1.6 eV in second-derivative spectra). Indeed, at $\theta = 1$, the intensity of the 1.2-eV transition peak is reduced to that of the background.

3. uv photoemission studies

The lowest panel of Fig. 5 shows a UPS spectrum obtained from a clean $SrTiO_3$ (100) 1 × 1 surface at room temperature. The spectral features are in good agreement with those of previous work.[1,4] The band-gap states are clearly visible. Upon deposition of platinum, the bulk band features from $SrTiO_3$ are

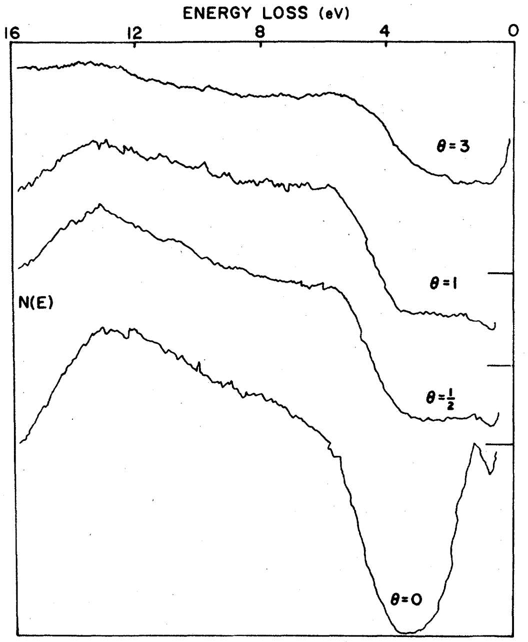

FIG. 4. Electron-energy-loss spectra of the $SrTiO_3$ surface with different coverages of platinum. The primary electron energy is ~100 eV.

attenuated. Also, there is an overall increase in the emission around the Fermi level, showing the transition from semiconductor to metallic behavior.

Following the procedure of Margaritondo *et al.*,[14] we computed and plotted the energy positions of the vacuum level and the conduction-band minimum as a function of average platinum coverage, as shown in Fig. 6. The clean $SrTiO_3$ (100) surface has a work function of 4.2 eV, with the Fermi level 0.2 eV above the conduction-band minimum. For the reduced crystal that we used, the Fermi level is approximately coincident with the bulk conduction-band minimum. Therefore, the bands bend downward by about 0.2 eV. This result is consistent with that of Henrich *et al.*[4] The work function increases steadily upon platinum deposition and levels off between $\frac{1}{2}$ and 1 monolayer. With further deposition, the work function gradually approaches that of the clean metal. The conduction-band minimum moves up by about 0.6 eV as the platinum coverage increases from zero to one monolayer. Beyond one monolayer, the $SrTiO_3$ bulk valence-band peaks are attenuated substantially and sit on top of an increasing secondary electron background so that their energy positions are difficult to locate. The band bending beyond one monolayer is not accurately measurable and therefore not indicated in Fig. 6.

IV. DISCUSSION

The decrease of the Sr(65 eV) to Ti(380 eV) Auger-peak ratio and the constancy of the O(510 eV)

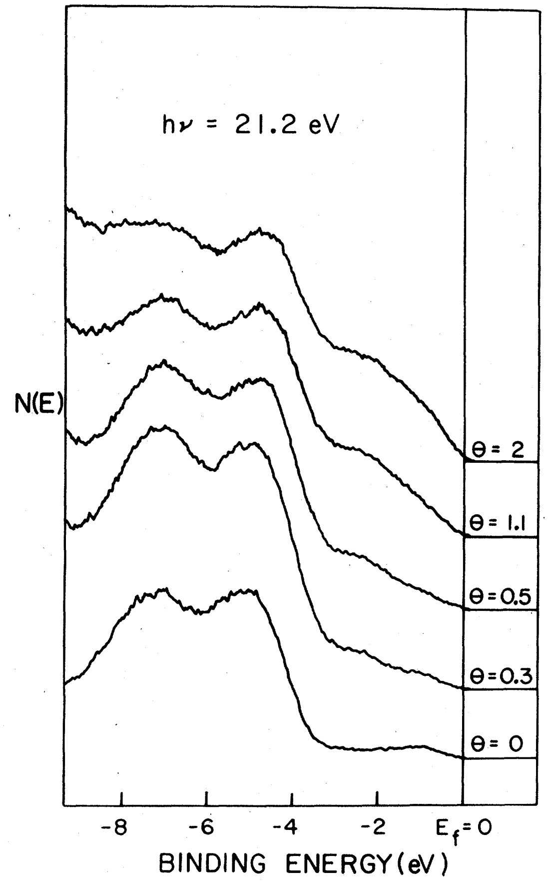

FIG. 5. uv photoemission spectra of the $SrTiO_3$ surface with different coverages of platinum. The energy resolution is about 0.3 eV.

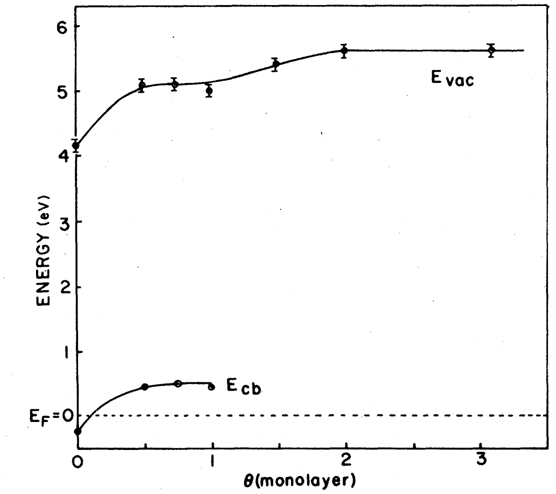

FIG. 6. Variation of the energy positions of the conduction-band minimum E_{cb} and the vacuum level E_{vac} relative to the Fermi level as a function of platinum coverage θ.

to Ti(380 eV) Auger-peak ratio as the temperature is raised beyond 240 °C are most interesting. By considering the $SrTiO_3$ crystal as being composed of alternating TiO_2 and SrO layers oriented in the [100] direction, one possible explanation for the above observation is the inward displacement of strontium ions (i.e., away from the surface) relative to the TiO_2 layers and the in-plane oxygen anions as the temperature of the $SrTiO_3$ surface is increased above 240 °C. Clearly, it would be interesting to verify this proposed explanation by performing a dynamical analysis of LEED intensity versus electron-energy profiles from the $SrTiO_3$ (100) 1×1 surface below and above the observed transition temperature.

The titanium A to B Auger-peak ratio increases with decreasing temperature. Henrich *et al.*[4] found that this peak ratio is a measure of the surface concentration of Ti^{3+} ions. This implies that the surface Ti^{3+} concentration becomes higher as the crystal temperature is lowered. From Fig. 2, there is some correlation between the variation of the Sr to Ti and the titanium A to B Auger-peak ratios as a function of temperature. It appears that the presence of Sr in the neighborhood of the TiO_2 layer promotes and stabilizes the formation of Ti^{3+} on the surface.

Platinum deposition on the $SrTiO_3$ (100) 1×1 surface results in peak shape changes of the Ti Auger peaks around 410 eV. On the other hand, the Sr Auger peaks are merely attenuated. The Pt Auger peak at 62.5 eV shifts upward to 64 eV as the average Pt coverage is increased from 1 to 3 monolayers. Since the generation of the Pt (63 eV) Auger electrons involves the Pt valence band, the above observation shows that the Pt valence band is not completely developed at one monolayer.[15] A further implication is that large Pt clusters are not formed at $\theta = 1$. The preservation of the 1×1 LEED pattern at $\theta = 1$ indicates that there is some degree of ordering of the Pt overlayer on the $SrTiO_3$ (100) surface.

Upon Pt deposition, the surface Ti^{3+} species are removed, as evidenced by the disappearance of the 1.2-eV electron-energy-loss spectroscopy (ELS) transition. The marked increase of the work function from 4.2 eV at $\theta = 0$ (clean surface) to 5.0 eV at $\theta = 1$ shows that there is an electron transfer from $SrTiO_3$ to Pt. These two results combine to indicate that Ti^{3+} species are removed by losing electrons to the Pt. This builds up a dipole layer across the Pt-$SrTiO_3$ interface and a Schottky barrier is formed. At $\theta = 1$, the Schottky barrier height (equal to the conduction-band minimum at the surface minus the Fermi level) is 0.4 eV. For the $SrTiO_3$ crystal we used, the electron concentration is on the order of $10^{19}/cm^3$. The width of the depletion region for a band bending ~ 0.5 eV is estimated to be several hundred angstroms. Therefore, in order for an electron to be transported from $SrTiO_3$ to Pt, the electron has to climb over a barrier of 0.4 eV, a difficult process at room temperature without an external potential. However, in the Pt-$SrTiO_3$ composite electrode experiment of Wrighton *et al.*[9], hydrogen is liberated from the Pt surface when the semiconductor side is illuminated by band-gap radiation, indicating an electron flow from the $SrTiO_3$ to the Pt surface. This can be explained by the fact that the band bending at the electrolyte ($5N$ NaOH)–semiconductor interface is ~ 1 eV before light illumination. With light illumination, electrons are generated, thereby reducing the band bending at both the electrolyte-$SrTiO_3$ and Pt-$SrTiO_3$ interfaces. It is then possible for the bands at the Pt-$SrTiO_3$ interfaces to be flattened (and therefore the Schottky barrier to disappear) while maintaining a sufficient band bending (~ 0.5 eV) at the $SrTiO_3$-electrolyte interface for efficient photoelectrolysis.

Clearly, the electronic properties of a metal-semiconductor interface depend on the structure, composition, and local interactions at the interface.[14,16–18] Therefore, it is possible to produce Pt-$SrTiO_3$ interfaces with widely different properties by manipulating the $SrTiO_3$ surface conditions during Pt depositions, e.g., surface orientation, stoichiometry and defect concentration, substrate temperature during deposition, etc. This can lead to fabrication of composite electrodes with better photoelectrolysis efficiencies.

The charge exchange between $SrTiO_3$ and Pt may also be important in photoinduced reactions because it controls the surface Ti^{3+} concentration, which in turn plays a determining role in chemisorption. For example, surface Ti^{3+} species promote the dissociative adsorption of water on titanium oxide surfaces.[8] We believe that by properly adjusting the surface Ti^{3+} species using submonolayer metal coverages, one can optimize and control the product distribution and the course of a given chemical reaction, e.g., the photocatalytic reaction of CO_2 and H_2O to give methane on $SrTiO_3$ surfaces.[12] We are currently studying other types of metal-semiconductor interfaces with this objective.

V. CONCLUSIONS

On the clean $SrTiO_3$ (100) surface, the strontium Auger peak at 65 eV decreases abruptly as the temperature is raised beyond 240 °C. LEED shows that there is some degree of ordering when Pt is deposited on the $SrTiO_3$ (100) surface. Platinum deposition results in the removal of surface Ti^{3+} and the formation of a Schottky barrier at the metal-semiconductor interface, the barrier height at one monolayer Pt being 0.4 eV. It is of importance to attempt producing Pt-$SrTiO_3$ interfaces with different electronic properties and surface Ti^{3+} concentrations, which appear to play a vital role in photoelectrolysis, chemisorption, and photoinduced reactions.

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