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Auger and photoemission investigations of the platinum-$SrTiO_3$(100) interface: Relaxation and chemical-shift effects

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The energies of the core levels and of the Auger peaks have been measured for the Pt-$SrTiO_3$(100) interface with different coverages of platinum. By comparing the core level and Auger chemical shifts for Pt, the changes in the total relaxation energy was obtained with different coverages of platinum. The chemical shift found for Pt-4*f* peaks, after taking into account relaxation energy, indicates transfer of charge on the order of 0.6 electron/Pt atom from $SrTiO_3$ to platinum.

I. INTRODUCTION

In recent years, various investigators have shown considerable interest in the use of different semiconducting metal-oxide electrodes to photoelectrolyze water under band-gap illumination.[1] Out of the various such semiconductors used for photoelectrolysis, titanium dioxide (TiO_2) and strontium titanate ($SrTiO_3$) are the most extensively studied, due to the fact that they remain chemically stable under anodic polarization. For monochromatic ultraviolet light (≃330 nm), optical to chemical energy conversion is on the order of 30% for the $SrTiO_3$-based cells under optimum bias conditions.[2] Wrighton *et al.* further demonstrated recently that a platinized $SrTiO_3$ surface is capable of evolving H_2 in the dark at a potential more positive than O_2 evolution in the light.[3] It is interesting to point out that $SrTiO_3$ alone is not capable of evolving H_2 at the thermodynamic potential and it is the Pt coating that reduces the H_2 overvoltage enough to allow the photoelectrolysis of water.[3]

In spite of the extensive studies on the use of TiO_2 and $SrTiO_3$ as electrodes for the photoelectrolysis of water, few attempts have been made to characterize the surface composition and electronic properties of these materials under various experimental conditions, in particular, the electronic interaction when Pt is in contact with $SrTiO_3$. Sayers and Armstrong have recently shown from ESCA studies that prolonged photoelectrolysis by these electrodes results in the decrease of Ti^{3+} species and increase of oxygen concentration on the semiconducting electrode surface.[4] Other elecchemical studies indicated that this leads to loss of photoelectrolysis activity and even corrosion.[5] These results strongly suggest the importance of Ti^{3+} ions present at the surface of $SrTiO_3$ or TiO_2 electrodes in the photoelectrolysis of water. Recently, theoretical calculations on the Pt-TiO_2 system by Horsely[6] have shown that there is a strong interaction between Pt and Ti, resulting in the transfer of electron from Ti to Pt atom.

As part of our systematic studies on the surfaces of semiconductors[7] used for photoelectrolysis of water, we report here Auger, ESCA, and UPS (ultraviolet photoemission) studies on the Pt-$SrTiO_3$ (100) interface. The main object of these investigations is to study the interaction between Pt and $SrTiO_3$ surface by analyzing the various changes observed in Auger, ESCA, and UPS.

II. EXPERIMENTAL

The measurements were performed using a Physical Electronics PHI 548 ESCA/Auger analysis system.[7] The system is equipped with an Mg $K\alpha$ x-ray tube, ion gun, LEED optics, and a differentially pumped cold-cathode He discharge lamp. The specimen used was a 99.99% undoped strontium titanate single crystal. Samples with (100) orientation as determined by Laue back reflection techniques were cut and polished down progressively to a smoothness of 0.03 μm using Al_2O_3 powders. The samples were then mounted on a ceramic holder which had a tungsten filament mounted behind the crystal to facilitate radiation heating of the crystal. In order to reduce the charging effect caused by the emission of photoelectrons from $SrTiO_3$ in UPS and ESCA experiments, all crystals used in this experiment were reduced by heating in vacuum to 450 °C for 5 h. For argon ion sputtering of the $SrTiO_3$ surface, the vacuum chamber was filled with argon to a pressure of 5×10^{-5} Torr. A 2-kV–25-μA argon ion beam was used to sputter clean the specimen at room temperature. Subsequent annealing at 450 °C for 40 min gave rise to a sharp $SrTiO_3$(100)-1×1 LEED pattern.

All UPS and XPS spectra were taken with a PHI model 15–250 G double pass cylindrical mirror analyzer operating in the large aperture mode and at a pass energy of 25 eV. The pressure in the main spectrometer chamber was on the order of

6×10^{-9} Torr when these spectra were acquired.

Pt was evaporated by placing the $SrTiO_3$ crystal surface in front of a self-made evaporator. The Pt coverage was measured by means of a quartz crystal thickness monitor positioned at the same angle and distance as the $SrTiO_3$ sample. The monitor was previously calibrated by observing the percentage attenuation in the oxygen Auger peak at 510 eV as a result of Pt deposition, assuming a mean free path of 11 Å for 510-eV electrons. The calibrated value was in good agreement with the theoretical value deduced from the quartz crystal constant, assuming that one platinum monolayer ($\theta = 1$) is equal to 1.6 $\times 10^{15}$ Pt at./cm^2.

In XPS (x-ray photoemission), it is important to be able to establish a meaningful reference level to set the energy scale. In the present study, the sample holder is shorted to the analyzer. Therefore, the binding energy $E_B(E_F = 0)$ relative to the Fermi energy E_F of the analyzer is given by

$$E_B(E_F = 0) = h\nu - E_e - e\varphi_A , \tag{1}$$

where $h\nu$ is the photoelectron energy, E_e is the electron kinetic energy, and φ_A is the analyzer work function. However, in a semiconductor or insulator, E_F is not the best reference level. Shift of E_F due to changes in band bending can occur. Moreover, in insulators and semiconductors, charging of the sample can contribute to changes observed in the binding energies. To avoid these problems, the present studies make use of an internal reference. All binding energy values are measured with respect to the valence-band maximum (VBM), assuming a constant Sr $3d_{5/2}$ level of 129.5 eV with respect to the VBM of the strontium titanate (100) surface.

III. RESULTS AND DISCUSSION

A typical Ti-$2p_{3/2,1/2}$ spectrum for the clean ordered $SrTiO_3(100)$ 1×1 surface is shown in Fig. 1. An energy separation of 5.8 eV observed between the Ti-$2p_{3/2}$ and Ti-$2p_{1/2}$ peaks in the present studies is in close agreement with that reported by Murata *et al.*[8]

Figure 2 shows the XPS spectra of Pt-$4f_{7/2,5/2}$ peaks as the Pt coverage on the $SrTiO_3$ surface is gradually increased. It appears that Pt-$4f$ peaks move towards lower binding energy as the platinum coverage increases. The Pt-$4f_{5/2}$ peak shifts towards the low-energy side by an average of 0.3 eV as the platinum coverage increases from 0.4 to 15 monolayers (bulk). Within experimental error, the oxygen $1s$ and titanium $2p$ core levels show no shift relative to the valence-band maximum of the $SrTiO_3(100)$ surface.

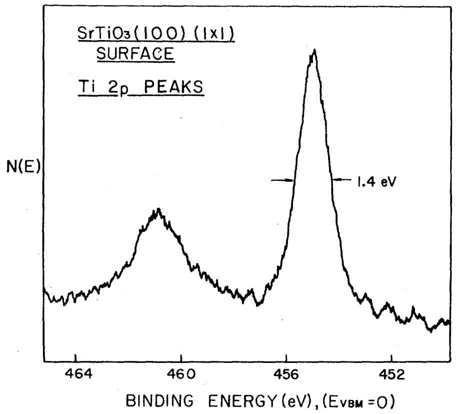

FIG. 1. The $2p_{3/2,1/2}$ spectrum of titanium from a clean $SrTiO_3(100)$ 1×1 surface.

The shift in binding energy ΔE_B relative to the Fermi level can be written as

$$\Delta E_B(E_F = 0) = \Delta E - \Delta R + \Delta E_{BB} , \tag{2}$$

where ΔE is the shift due to the initial state charge distribution, ΔR is that due to the rearrangement of the electrons to screen the positive hole resulting from photoionization, and ΔE_{BB} the band-bending shift. The sign of ΔE_{BB} (+ or −) depends on which direction (downward or upward, respectively) the band bends. However, shift due to band bending can be taken into account by calibrating all spectra with respect to the valence-band maximum as described previously. Therefore, the shift in binding energy ΔE_B relative to the VBM is given by

$$\Delta E_B(E_{VBM} = 0) = \Delta E - \Delta R . \tag{3}$$

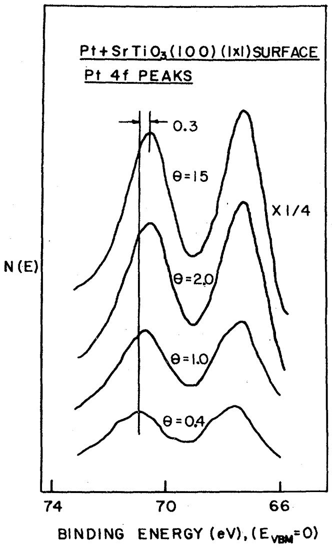

FIG. 2. The Pt-$4f_{7/2,5/2}$ spectrum with different coverages of Pt over $SrTiO_3(100)$ 1×1.

In the following section, an attempt is made to differentiate the contributions of various factors included in Eq. (3) to the experimentally observed ΔE_B.

A. Relaxation energy

The Auger electron energy depends on all the factors mentioned in Eq. (3) for the core-level shift. For the Auger kinetic energy K, the corresponding expression is approximately given by

$$\Delta K = -\Delta E + 3\Delta R \, . \tag{4}$$

The sum of the core-level shift ΔE_B and Auger kinetic energy shift ΔK is therefore equal to $2\Delta R$, or twice the contribution of relaxation energy to the core binding energy shift. It should be noted that the factor 2 depends on the assumption of constant polarizability of the surrounding medium[9] [in the classical derivation of expressions (3) and (4)] or on the assumption that certain different Coulomb matrix elements are equal to one another (in the quantal derivation).[10] Experimental evidence suggests that it might be as large as 3.[11]

Therefore, in order to find the contribution of relaxation energy, shift in the Auger spectra of Pt was studied as the platinum coverage varies over the $SrTiO_3(100)$ surface. Figure 3 shows the Auger spectra of platinum and oxygen. A careful analysis of the shift in the Pt NNN Auger peak at 165 eV with respect to oxygen indicates a shift of 1.9 eV towards higher kinetic energy as the Pt coverage increases from 0.4 monolayer to 15 monolayers (bulk). UPS studies (Fig. 4) of the initial stages of the Pt deposition show no significant electron population at the Fermi level, indicating that no large Pt islands are formed at low coverage. Therefore, the change in electronic relaxation energy ΔR for platinum as the Pt coverage increases from 0.4 monolayer to 15 monolayers derived from a comparison of the Auger energies and core-ionization energies (using the factor of 2 discussed above) is calculated to be 0.8 eV. This was indeed expected since with increased platinum deposition, more Pt atoms are attached to another Pt atom than atoms in $SrTiO_3$.

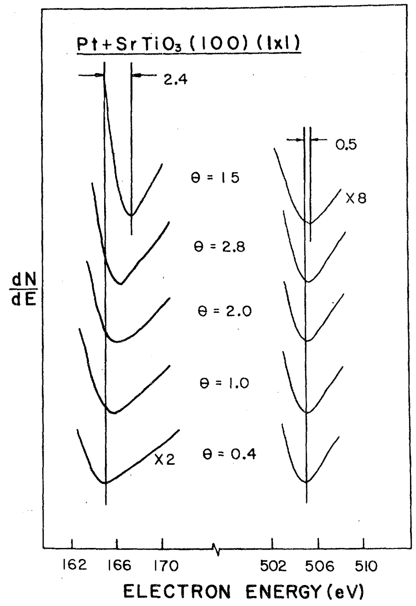

FIG. 3. Auger electron spectra of platinum and oxygen from the $SrTiO_3(100)$ 1×1 surface with different coverages of platinum.

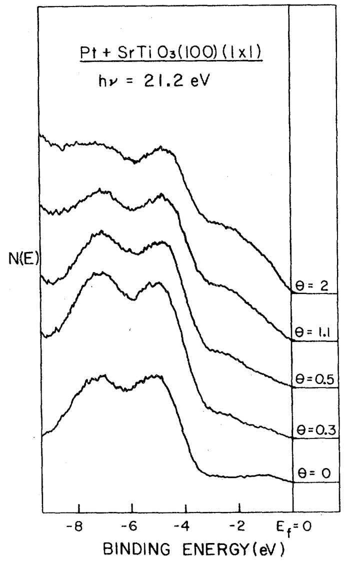

FIG. 4. HeI photoemission spectra of the $SrTiO_3$ surface as a function of Pt coverage.

B. Initial-state charge distribution (chemical shift)

The contribution of initial-state charge distribution to the core-level shift of Pt can be estimated from Eq. (3) if all the other quantities are known. The shift observed in the Pt-$4f$ peak binding energy due to relaxation and initial-state configuration comes out to be -0.3 eV. Since the corresponding contribution of relaxation energy shift has been shown to be $+0.8$ eV, the shift due to initial-state charge distribution from Eq. (3) is therefore equal to $+0.5$ eV. This positive energy shift as one moves from low coverage (0.4 monolayer) to bulk (15 monolayers) indicates that a platinum atom at low coverage carries a negative charge with respect to bulk platinum atoms. These results imply that with platinum deposition, there is an electron transfer from $SrTiO_3$ to the platinum.

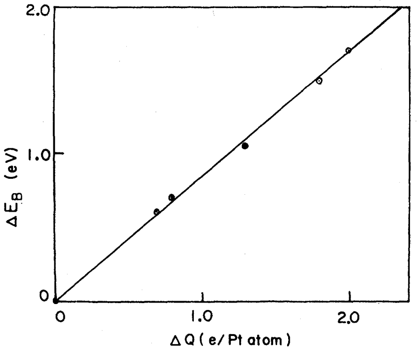

FIG. 5. The experimental chemical shift (ΔE_B) vs the charge per platinum atom.

In order to derive a quantitative picture for the amount of electron transfer from $SrTiO_3$ to Pt, one has to correlate the binding energy shift in Pt core levels due to initial-state charge redistribution to the amount of charge increase or decrease on platinum. Unfortunately, such a correlation between chemical shift (after taking relaxation into account) and the charge on Pt is not available in the literature. However, a rough guess can be made by relating the observed Pt core level shift with the charge on platinum for those platinum compounds where relaxation energy is not expected to vary much from compound to compound. Figure 5 shows such a relation between the platinum core-level shift and the charge transfer as derived from the data of Cook *et al.*[12] The derived chemical shift of -0.5 eV for Pt in the Pt-$SrTiO_3(100)$ interface indicates that there is an electron transfer from $SrTiO_3$ to Pt corresponding to (0.6 ± 0.1) electron/Pt atom (Fig. 5). Recently, Horsley[6] has done theoretical calculations for the Pt-TiO_2 system. Since the nearest neighbors of Ti in $SrTiO_3$ are similar to those in TiO_2 and the strontium lowest empty and highest occupied electronic levels are far away from the Fermi level, one expects that the charge transfer behavior between the metal and the semiconductor is similar for both the Pt-$SrTiO_3$ and Pt-TiO_2 systems. Horsley showed that there is an electron transfer from Ti to Pt, in agreement with the present experimental results. It is shown further that the amount of electron transfer from Ti to Pt in the case of reduced TiO_2 is 0.6 electron/Pt atom, cf. the value of 0.6 ± 0.1 derived from our present work.

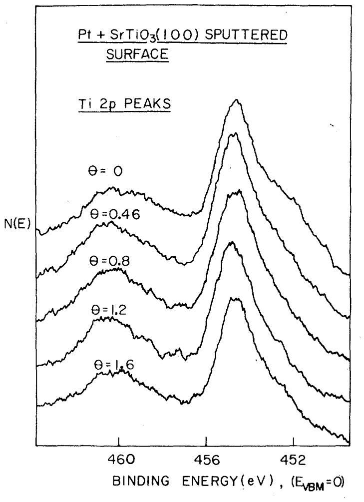

FIG. 6. Ti-$2p_{3/2,1/2}$ spectra from the sputtered $SrTiO_3(100)$ surface with different coverages of platinum.

Recent studies in this laboratory on the Pt deposition on sputtered $SrTiO_3(100)$ surface further confirm the charge transfer from $SrTiO_3$ to the platinum atom. Figure 6 shows Ti-$2p_{3/2,1/2}$ spectra for the sputtered $SrTiO_3(100)$ surface with different coverages of platinum. It is to be noted from Fig. 6 that the shoulder on the low-energy side of the Ti-$2p_{3/2}$ peak, which corresponds mainly to the Ti^{3+} species, decreases with increase in platinum coverage. The decrease in shoulder is quite remarkable with the first coverage (0.46 monolayer) of platinum. These results indicate that platinum deposition converts Ti^{3+} species at the surface of sputtered $SrTiO_3(100)$ to Ti^{4+}, thus implying transfer of electrons from $SrTiO_3$ to the platinum atom. A detailed analysis of these results will be discussed in the forthcoming communication.

ACKNOWLEDGMENTS

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