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**STUDIES OF METAL - SEMICONDUCTOR INTERFACES
IN CATALYSIS AND ENERGY CONVERSION**

Annual Report

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ABSTRACT

We completed the installation of a multiple-technique surface analytical system, capable of Auger, photoemission (UPS and XPS), low energy electron diffraction, thermal desorption and thin film evaporation studies. An isolation cell attachment has been designed for high pressure gas phase (1 to 1000 torr) reaction studies.

By depositing nickel onto a clean ordered $\text{TiO}_2(110)$ surface held at room temperature, we were able to obtain an ordered overlayer as evidenced by LEED. Both energy loss and UV photoemission studies showed that there is an electron transport from nickel to TiO_2 , resulting in an increase of the surface Ti^{3+} concentration and the formation of an accumulation layer on the $\text{TiO}_2(110)$ surface. In addition, UV photoemission results suggested that the Ni atoms and the surface Ti^{3+} are well dispersed on the TiO_2 surface.

Auger studies on the clean $\text{SrTiO}_3(100)\text{-}1\times 1$ surface showed that the strontium Auger signal decreases abruptly as the temperature is raised beyond 240°C . We believe that this is a result of the outward displacement of the topmost TiO_2 layer relative to the second SrO layer. Platinum deposition on the $\text{SrTiO}_3(100)\text{-}1\times 1$ surface results in the removal of surface Ti^{3+} and the formation of a Schottky barrier at the interface. This result is discussed in light of the recent findings in photoelectrolysis.

1. INTRODUCTION

The format of this report is as follows. In section 2, we will briefly describe the installation of the experimental system where we performed most of our research studies. In section 3, we summarize the results obtained on the Ni-TiO₂(110) system. In section 4, the preparation and electronic properties of the Pt-SrTiO₃(100) Schottky barrier will be described.

2. INSTALLATION OF THE EXPERIMENTAL SYSTEM

The bulk of the work was done on a Physical Electronics model 548 system, which arrived at Northwestern University in July, 1978. The basic system is equipped with a double-pass cylindrical mirror analyzer, a coaxial electron gun for Auger and energy loss studies, a sputter-ion gun, low energy electron diffraction optics and a modified UV source for He I and He II photoemission studies. We added a quadrupole mass spectrometer (funds from ACS Petroleum Research Fund), a gas manifold system and an evaporator for platinum and nickel evaporation. We are in the process of installing a magnesium K α X-ray source for X-ray photoemission studies. In addition, with the help of Northwestern University's chemistry electronics facility, we are building a micro-computer and interfacing it with the experimental system for data acquisition and signal averaging. This is especially important in X-ray photoemission studies because the signal levels in such measurements are usually very low. Finally,

we are in the process of completing an isolation cell attachment by means of which a specimen can be transferred back and forth between the UHV chamber and a small reaction chamber. The specimen can be prepared, characterized in the UHV chamber and retracted back into the reaction chamber, which can be isolated from the UHV chamber using a gate valve and in which high pressure (1 - 1000 torr.) reactions can be studied.

3. STUDIES OF THE Ni-TiO₂(110) INTERFACE

As indicated in our initiation proposal, the Ni-TiO₂(110) interface is a good model system for methanation catalysts. We have been successful in growing ordered Ni overlayers on top of a clean ordered TiO₂(110)-1x1 surface. The deposition was accomplished using a home-made evaporator. The average Ni coverage θ was estimated from the attenuation of the TiO₂ bulk energy loss peaks and the growth of Ni Auger peaks. The specimen was held at around room temperature during evaporation.

Figure 1 shows the energy loss spectra of the TiO₂(110) surface with different Ni coverages. The clean ordered TiO₂(110) surface shows distinct loss peaks at 1.2, 6.0, 10.3 and 13.1 eV, in agreement with previous work^(1,2). The most notable change with increasing nickel coverage is an overall increase in the background in the energy loss range of 0.8 - 3.5 eV⁽³⁾, suggesting that the surface becomes metallic with nickel deposition. At low coverages (θ less

Fig.1 Energy loss spectra from the $\text{TiO}_2(110)$ surface with different average coverage of Ni (θ in monolayers). The incident electron energy used is about 100 eV. The spectra were obtained using pulse counting with an energy resolution of 0.35 eV.

Fig.2 UV photoemission spectra from the $\text{TiO}_2(110)$ surface with different Ni^{2+} coverages. The energy resolution is 0.3 eV.

than 0.2 monolayer), there is an indication that there is an energy loss transition occurring at 1.2 eV, which gets obscured at higher Ni coverages. Previous work demonstrated that the 1.2 eV transition (1.6 eV in second derivative spectra) is a fingerprint for the existence of surface Ti^{3+} species^(1,2,4). It appears that Ni deposition on the TiO_2 (110) surface results in the formation of Ti^{3+} .

Figure 2 shows the He I photoelectron spectrum of the TiO_2 (110) surface as a function of θ in monolayers. The clean TiO_2 (110)-1x1 surface shows two prominent valence band peaks at 5.0 and 7.7 eV below the Fermi level, in excellent agreement with the results of Chung et al⁽¹⁾ and Henrich et al⁽⁴⁾. A weak band gap emission is observable. Upon nickel deposition, this band gap emission increases. At $\theta = 0.2$, a weak peak at 0.5 - 0.6 eV below the Fermi level is clearly discernible. Previous studies suggest that this band gap emission is due to surface Ti^{3+} species. Therefore, in agreement with the findings of energy loss spectroscopy, surface Ti^{3+} species are formed as a result of nickel deposition on the TiO_2 surface.

Figure 3 shows the movement of various band edges as a function of θ . Nickel deposition causes the work function to decrease, the valence and conduction band edges to bend downwards. At $\theta = 1$, the Fermi level is 0.6 eV above the conduction band minimum, indicating the formation of an accumulation layer at the Ni- TiO_2 interface as a result of electron flow from nickel to titanium dioxide. It appears

Fig.3 Variation of the energy positions of the vacuum level and the conduction band minimum for the $TiO_2(110)$ surface as a function of θ .

that Ti^{3+} species are formed by the Ti^{4+} in TiO_2 accepting electrons from nickel. Note that the changes of work function and band-bending level off at $\theta = 0.5$, indicating a strongly local interaction between Ni and TiO_2 at the interface. Other metal-semiconductor interface studies show similar observations that the first metal overlayer determines the overall electronic properties of the interface^(5,6,7). Up to one monolayer of nickel, the surface is still not metallic as evidenced from the UPS spectrum of the $\text{TiO}_2(110)$ surface at $\theta = 1$. This suggests that both the nickel atoms and the surface Ti^{3+} are well dispersed on the TiO_2 surface. Finally, both energy loss and photoemission studies show that spectral features arising from TiO_2 are not affected significantly by the Ni overlayer, indicating that there is no significant chemical reaction occurring between TiO_2 and Ni.

4. STUDIES OF THE Pt-SrTiO₃(100) SCHOTTKY BARRIER

We carried out an exhaustive study on the dependence of the Sr, Ti and O Auger intensities measured from a $\text{SrTiO}_3(100)\text{-}1\times 1$ surface as a function of temperature. The result is shown in figures 4 and 5. One interesting finding is the drop of the Sr(65 eV)/Ti(380 eV) Auger peak ratio as the temperature is raised beyond 240°C. Similar observations have been made on the $\text{SrTiO}_3(111)$ surface⁽⁸⁾. On the other hand, the O(510 eV)/Ti(380 eV) Auger ratio stays constant and the Ti(A)/Ti(B) ratio increases monotonically as the temperature is raised from 100 to 350°C. All these

Fig.4 The Auger electron spectrum obtained from a $\text{SrTiO}_3(100)-1 \times 1$ surface at room temperature. The beam energy used is 2000 eV and the spectrum is obtained at a peak-to-peak modulation of 3 to 4 volts.

Fig.5 Variation of Auger peak ratios obtained from the $\text{SrTiO}_3(100)-1 \times 1$ surface as a function of the crystal temperature.

changes are reversible as a function of temperature.

It is difficult to explain all the above observations as due to changes in the strontium surface concentration. Rather, we believe that this is a result of the outward displacement of the topmost TiO_2 layer relative to the second SrO layer (remember that one can consider a SrTiO_3 crystal as being composed of alternating TiO_2 and SrO layers oriented in the $[100]$ direction). Assuming a mean free path of $4 \text{ \AA}$ for 65 eV electrons, one needs a displacement of only $0.35 \text{ \AA}$ to account for the observed change in the $\text{Sr}(65 \text{ eV})/\text{Ti}(380 \text{ eV})$ ratio. On the other hand, because of the larger mean free path of the oxygen 510 eV Auger electrons (about $10 \text{ \AA}$), the change in the $\text{O}(510 \text{ eV})/\text{Ti}(380 \text{ eV})$ Auger peak ratio is negligible. It would be interesting to verify this proposed explanation by performing a dynamical LEED analysis on the $\text{SrTiO}_3(100)$ surface as a function of temperature.

The titanium A/B Auger peak ratio changes in a parallel manner to the Sr/Ti ratio. It was found previously that the titanium A/B peak ratio is a measure of the surface concentration of Ti^{3+} ions^(9,10). It therefore appears that the presence of strontium in the neighborhood of the TiO_2 layer promotes and stabilizes the formation of Ti^{3+} on the surface. This may be contrasted with the case of titanium dioxide in which a titanium dioxide (110) or (100) surface can be produced without surface Ti^{3+} species.

Platinum deposition was performed in a way similar to nickel. The average platinum coverage was estimated from the attenuation of the oxygen Auger peak at 510 eV and the growth of the platinum Auger peaks. The SrTiO_3 crystal was held at about 30°C during deposition. Figure 6 shows the evolution of the Auger spectrum in the energy range of 0 to 150 eV and 300 - 450 eV as a function of θ , the platinum coverage in monolayers. Note the growth of the platinum Auger peaks at 42 and 63 eV with increasing θ . Careful measurements show that as θ increases from 1 to 3 monolayers, the Pt Auger peak at 62.5 eV shifts upward to 64 eV. Since the generation of the Pt(64 eV) Auger electrons involves the Pt valence band, the above observation implies that the Pt valence band is not completely developed at one monolayer⁽¹¹⁾, indicating that large Pt clusters are not formed. A distinct 1×1 LEED pattern from the $\text{SrTiO}_3(100)$ surface is still preserved at $\theta = 1$, suggesting partial ordering of the Pt overlayer on the $\text{SrTiO}_3(100)$ surface.

Energy loss spectroscopy studies shows that Pt deposition removes surface Ti^{3+} , as evidenced from the disappearance of the 1.2 eV loss peak as θ increases (fig.7). UPS shows that the work function increases from 4.2 eV to 5.0 eV as θ increases from zero to one monolayer (fig.8). This is consistent with the fact that Ti^{3+} species are removed by losing electrons to the Pt. The Schottky barrier height at $\theta = 1$ is 0.4 eV. Therefore, in order for an electron to be

Fig.6 Evolution of the SrTiO₃ Auger spectrum with increasing Pt coverage. All the spectra were obtained at an electron incident energy of 2 kV and at room temperature.

Fig.7 Electron energy loss spectra obtained from the SrTiO_3 (100)-1x1 surface as a function of platinum coverage. The incident electron energy used is about 100 eV. The spectra were obtained in the electron counting mode, at a resolution of 0.3 eV.

Fig.8 Variation of the energy positions of the vacuum level E_{vac} and the conduction band minimum E_{cb} for the SrTiO_3 (100) surface, as a function of the platinum coverage θ .

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⁽¹²⁾, hydrogen is liberated from the Pt surface when the semiconductor side is illuminated with 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) - SrTiO_3 interface is about 1 eV before light illumination. With light illumination, electrons are generated and a negative charge is built up in SrTiO_3 , thereby flattening the bands (fig.9). It is then possible

Figure 9

for the bands at the Pt- SrTiO_3 interface to be flattened and therefore the Schottky barrier to disappear while maintaining a sufficient band-bending (0.3-0.4 eV) at the SrTiO_3 -electrolyte interface for efficient photoelectrolysis.

5. PUBLICATIONS BASED ON THE PRESENT CONTRACT

"Surface Spectroscopy Studies of the $\text{SrTiO}_3(100)$ surface and the Pt- SrTiO_3 Interface", by Y. W. Chung and W. B. Weissbard, submitted to Physical Review, February 1979.

6. MISCELLANEOUS

Time devoted by the Principal Investigator :

100 % time for one summer month (1978)

20 % time for the academic year

REFERENCES

1. Y.W.Chung, W.J. Lo and G.A.Somorjai, Surf.Sci. 64,588(1977)
2. W.J.Lo, Y.W.Chung and G.A.Somorjai, Surf.Sci.71,199(1978)
3. For energy losses less than 0.8 eV, the elastic peak dominates.
4. V.E.Henrich et al, Phys.Rev.Lett. 36,1335(1976)
5. J.E.Rowe et al, Phys.Rev. B15,2195(1977)
6. Y.W.Chung,W.J.Siekhaus and G.A.Somorjai,Phys.Rev. B15,959(1977)
7. P.W.Chye et al, Phys.Rev. B18,5545(1978)
8. W.J.Lo and G.A.Somorjai, Phys.Rev. B17,4942(1978)
9. V.E.Henrich et al, Phys.Rev. B17, 4908(1978)
10. S.Thomas, Surf.Sci. 55,754(1976)
11. R.C.Baetzold, J.Appl.Phys. 47,3799(1976)
12. M.S.Wrighton et al, J.Sol.St.Chem. 22,17(1977).