Gas Sensing Characteristics of Ultrathin TiO_{2-x} Films Investigated with XPS, TPD and *In Situ* Resistance Measurements[†]

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Ultrathin Pt/TiO_{2-x} sensing films are characterized to investigate the adsorption and reaction processes that cause resistance changes. The films are prepared by oxidizing films with a nominal thickness of 65 Å Pt on top of 65 Å Ti at temperatures of 800–900 K. Scanning electron microscopy (SEM) shows that after the high-temperature oxidation the film structure becomes discontinuous. The film resistance is very responsive to oxygen exposure in the 500–700 K range, giving an increase in the film resistance. Thermal desorption studies suggest that oxygen exposure in this temperature range causes the incorporation of surface and lattice oxygen. The sensitivity to reducing gases such as hydrogen or propylene becomes very pronounced after subjecting the Pt/TiO_{2-x} films to thermal treatment in oxygen in the 500–700 K range. Exposure to hydrogen or propylene at elevated temperatures leads to partial removal of surface oxygen and a decrease in film resistance. The trends in the relative resistance changes of Pt/TiO_{2-x} films as a function of gas exposure confirm that both platinum and TiO_{2-x} surface sites contribute to high gas sensitivity. Thermal treatment under a controlled atmosphere alters the interaction between platinum and titania, modifying the relative sensitivity of the discontinuous film to oxidizing and reducing gases. (© 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The objectives of the present study are to develop a method for investigating gas adsorption-induced resistance changes of ultrathin Pt/TiO_{2-x} films, to correlate *in situ* resistance measurements with temperatureprogrammed desorption (TPD) and to characterize the surface composition and microstructure of the films with XPS and environmental scanning electron microscopy (ESEM). The samples are equipped with fourpoint conductance probes, giving an opportunity to correlate surface conductance changes with microstructural and compositional changes. This characterization effort is useful for furthering the understanding of thin film-based chemical sensors.

Thin films of TiO₂ are used in combination with catalytic additives of platinum as chemically sensitive elements for microchemical sensors.¹ These types of sensors, which can be produced inexpensively using batch microelectronic thin-film technology, are capable of detecting both oxidizing and reducing gases through gas-induced resistance changes of the thin metal/metal oxide film. An ultrathin-film Pt/TiO_{2-x} microchemical sensor which detects ppm levels of oxygen and also responds to hydrogen and hydrocarbons has recently been reported by our research group.^{2,3}

The electrical properties of thin metal oxide films with dispersed, noble metal additives are controlled by the oxide stoichiometry, the film morphology and the nature of interfaces between metal and oxide particles. The presence of adsorbed species may alter the conductance of thin metal or metal oxide films by modifying the charge carrier concentration and change carrier mobility.⁴ In discontinuous metal films, the conductance depends on both particle size and relative spacing between metal particles.⁵ These microstructural properties may be altered with gas exposure.⁶ Two mechanisms that have been proposed for the conductance variations of semiconducting metal oxides due to gas exposure are:⁷ chemisorption-band bending effects and the creation (removal) of surface oxygen vacancy defects. Each mechanism involves charge transfer reactions and thus leads to a change in the concentration of free electrons.

EXPERIMENTAL

The thin-film samples, 1 cm^2 in size, are shown in Fig. 1. The samples were prepared by sequential e-beam evaporation of titanium and platinum onto a 4-inch fused quartz wafer. Typical nominal film thicknesses were 65 Å Ti and 65 Å Pt. A 4000 Å thick tantalum layer was sputter-deposited onto the backside of the quartz wafer to aid in the resistive heating of the samples. On top of the thin Pt/Ti film, photolitho-graphically defined electrodes consisting of 400 Å thick Ti covered with 1200 Å Pt were deposited in a four-point probe configuration for measuring film resistance. Hard-wire contacts were made to the electrodes with small tantalum clips. The sample temperature was mea-

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Figure 1. Schematic drawing of thin-film sample in top and cross-sectional view.

sured with a Chromel-Alumel thermocouple in contact with the quartz substrate.

The microstructure of the 65 Å Ti and 65 Å Pt film was examined *ex situ* before and after the experiments in an ultrahigh vacuum system (UHV). An environmental scanning electron microscope was used to acquire the SEM images. The instrument allows the examination of specimens in a gaseous environment. The images reported in this work were acquired in 5 Torr water vapor pressure. The pressure of a positive ion supply from the ionized gas ensures the suppression of negative charge build-up.⁸

Characterization of the films was performed in a UHV chamber operating at a base pressure of 1×10^{-9} mbar. The chamber, which has been described previously,9 was equipped with a residual gas analyzer (RGA), a dual anode Mg/Al x-ray source, a Leybold EA10 hemispherical electron energy analyzer and an XYZ manipulator. Α 10-pin thermocouple/ instrumentation feedthrough attached to the manipulator assembly was used for temperature and in situ resistance measurements. The sample could be heated in a constant current mode from room temperature to 900 K in 300 s and cooled from 900 K to 350 K in 15 min. Film resistance measurements were obtained by driving 200 μ A of current through the two outer conductance electrodes and measuring the voltage across the two inner electrodes. Gas adsorption studies were carried out by introducing research-grade gases into the chamber through a leak valve.

The XPS core-level spectra which are reported here were acquired using Mg K α radiation at 1253.6 eV. The x-ray source was at an incident angle of 35° from the surface normal. An analyzer pass energy of 100 eV was used for electron detection. All the XPS results are reported as binding energy (BE) of the emitted electrons. The binding energy scale calibration was verified using the binding energy position of surface carbon. The measured binding energy position of the C 1s line from indigenous surface carbon was 285 eV. This value is within experimental error of published values $(285 \pm 0.2$ eV).¹⁰ Atomic ratios were calculated from the areas under the Ti 2p, Pt 4f and O 1s photoemission peaks. Peak areas were measured by using a linear background baseline correction and were normalized by using published photoelectron cross-sections.¹⁰

RESULTS AND DISCUSSION

Film pretreatment and characterization

Before pretreating the 65 Å Ti/65 Å Pt film in controlled oxidizing and reducing environments to prepare a gas-sensitive film, an XPS spectrum of the film was obtained. The XPS spectrum of the freshly deposited 65 Å Ti/65 Å Pt film contained features originating from Pt, O and C, with no sign of any Ti, indicating that platinum and carbon completely cover the surface. The polymeric photoresist used in patterning of the electrodes is most likely the origin of much of the carbon contamination.

Stepwise pretreatment of the freshly deposited film consisted of initial oxidation in 1×10^{-6} mbar O₂ at 800–900 K for a period of 5 h, reduction in 10^{-6} mbar hydrogen for 30 min at 750 K and a final treatment in 1×10^{-6} mbar O₂ at 900 K for 1 h. The XPS spectra of the film following each of these treatments are shown in Fig. 2. The initial oxidation step removes most of the



Figure 2. The XPS spectra of the Pt/Ti film following: (a) initial oxidation at 800–900 K; (b) reduction at 750 K; (c) final oxidation at 900 K.

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carbon contamination of the surface such that platinum and titanium peaks are visible. Within experimental error, the binding energy of the Pt $4f_{7/2}$ line is characteristic for zero-valent platinum.¹⁰ The titanium surface consists of mainly TiO₂.¹¹ However, a small shoulder appears in the Ti 2p spectra at 457.2 eV which is char-acteristic of $Ti^{3+,11,12}$ An increase in the intensity of this shoulder is observed after reduction in H_2 at 750 K. The Ti³⁺ contribution to the total Ti 2p peak area increases from 10% to 24%. Following the last film oxidation step at 900 K, the Ti³⁺ contribution decreases to 4% of the total Ti 2p peak area, indicating that the titania is now nearly stoichiometric TiO_2 . After the final oxidation step, the Pt, Ti and O peaks appear to have shifted to slightly lower binding energies. This shift, although not well pronounced, was reproducible during the treatment of other thin-film samples. Following oxidation or reduction treatment of the films, there is no shift observed in the C 1s line used for charge referencing.

The effect of the pretreatments on the O/Ti and Ti/Pt ratios of the film is shown in Fig. 3. The O/Ti ratio goes through a minimum following the reduction step. The Ti/Pt ratio, on the other hand, shows a continuous increasing trend for each of the three treatment steps. This suggests that the relative surface concentration of Pt decreases during pretreatment, exposing more titanium on the surface.

An *ex situ* scanning microscopic characterization shows that the evaporated films are initially continuous [Fig. 4(a)]. However, after the three pretreatment steps involving oxidation at 800–900 K, reduction at 750 K and re-oxidation at 900 K, the films break up into islands about 500–1000 Å in size, many of them interconnected [Fig. 4(b)]. It is important to note that the microscope settings for Fig. 4(a) were identical to those used for Fig. 4(b) and the lack of fine structure in Fig. 4(a) is reproducible and not an imaging artifact.

Isothermal resistance measurements

The as-deposited 65 Å Ti/65 Å Pt film which was initially continuous had a resistance value of $\sim 50 \Omega$. The



Figure 3. The XPS area ratios for the Pt/Ti film following: (a) initial oxidation at 800–900 K; (b) reduction at 750 K; (c) final oxidation at 900 K.





(b)

Figure 4. Scanning electron micrographs of: (a) untreated Pt/Ti film, (b) pretreated Pt/TiO_x film.

resistance of the discontinuous film shown in Fig. 4(b) is much higher, typically of the order of several thousand ohms. The large increase in resistance is attributed to break-up of the film into islands and the increased concentration of titania at the surface. The pretreated films have negative temperature coefficients of resistance (TCR), characteristic of the discontinuous nature of these films.¹³

The response of the Pt/TiO_x film resistance to oxygen and reducing gases is shown in Figs 5 and 6. Exposure of a discontinuous Pt/TiO_x film to oxygen at 550 K causes an increase of ~1000 Ω in film resistance [Fig. 5(a)]. The resistance increase can be reversed by treating the oxygen-exposed films with H₂ at 550 K [Fig. 5(b)]. When the film is exposed to oxygen at the higher temperature of 620 K, a much more pronounced increase in resistance is observed [Fig. 6(a)]. After removal of gasphase oxygen, addition of C₃H₆ at 10⁻⁶ mbar and 575 K leads again to a reversal of the resistance change, closely restoring the film resistance to its original value [Fig. 6(b)].

The XPS spectra collected after each gas exposure step (shown in Figs 5 and 6) did not show any significant changes in the Ti 2p and 4f spectra. This suggests that the exposure times and temperatures used in these gas-sensing experiments do not cause significant modifi-

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Figure 5. Response of Pt/TiO_x film to: (a) O₂ at 550 K; (b) H₂ at 550 K.

cations in the average composition of the sensing film. It is conceivable that the interaction of the film with oxygen, hydrogen or propylene affects only the topmost surface layers but is still sufficient to alter the charge



Figure 6. Resistance changes of Pt/TiO_x film during exposure to: (a) O_2 at 620 K; (b) C_3H_6 at 575 K.

carrier concentration and/or mobility of the film. X-ray photoelectron spectroscopy measures a weighted average of several layers near the surface and samples a larger portion of the sensing film subsurface and bulk than more surface-sensitive methods such as ion scattering spectroscopy (ISS) and ultraviolet photoemission spectroscopy (UPS). Emission from the topmost surface layers of the film could not be detected due to overlap with the stronger signal from titania in remaining layers of the XPS sampling volume.

Molecular oxygen may react directly from the gas phase to anneal oxygen vacancies at the surface of titania and in subsurface regions which can be reached by diffusion.¹⁴ The platinum particles on the surface of the titania may act as catalyst for activation of oxygen which can then spill over to titania sites where it gets incorporated in the form of surface and subsurface lattice oxygen. Oxygen, hydrogen or hydrocarbon exposure of the films at elevated temperatures may alter the number of free electrons in the film. For instance, electron capture during annealing of surface and subsurface oxygen vacancies with atomic oxygen could cause an increase in overall film resistance. Platinum is also very effective in activating H_2 and propylene. These activated species may then react with the surface lattice oxygen and form surface hydroxyl groups. Hydrogen can also form titanium hydrides.

Temperature-programmed desorption and *in situ* resistance measurements

Oxygen TPD experiments were carried out with in situ resistance measurements. In these experiments, the film was sequentially exposed to 1×10^{-6} mbar oxygen at 185 K for 30, 60 and 90 s, respectively. After each oxygen exposure, the film temperature was linearly ramped from 185 to 875 K while monitoring the film resistance. The TPD and resistance results are shown in Fig. 7. A large desorption peak is observed at 225 K, followed by a smaller peak at ~ 400 K. As the temperature is increased further, a broad desorption feature persists up to 875 K. The first peak at 225 K is attributed to the desorption of molecular oxygen from platinum sites.¹⁵ The second peak at ~ 400 K is assigned to oxygen desorbing from titania. Typically, molecular oxygen desorbs from oxide surfaces between 300 to 400 K.¹⁶ The continuous oxygen desorption feature in the high-temperature region may be due to the removal of lattice oxygen from subsurface regions of the film, causing the creation of oxygen vacancies.17

The film resistance was measured *in situ* during each TPD run. The clean film shows a steep initial decline of resistance with temperature, leveling out between 300 and 400 K, followed by a second stepwise decline starting at 425 K. A similar discontinuity in the temperature dependence of resistance has been previously observed on titania¹⁸ and other oxides, such as SnO_2 .¹⁹ The resistance curve for the clean film proved to be reproducible after oxygen exposure and removal of oxygen by TPD. In the high-temperature regime between 600 and 875 K, the resistance curves for the oxygen-exposed films nearly coincide with that of the clean film, giving further proof that the films do not undergo significant changes in their overall characteristics during the

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Figure 7. Temperature-programmed desorption of O_2 with *in situ* resistance measurement. Oxygen exposures of 1×10^{-6} mbar for: (a) 0 s; (b) 30 s; (c) 60 s; (d) 90 s.

sequential TPD runs. There are, however, distinct differences in the lower temperature regime of the resistance curves as a function of the initial oxygen exposure. At 200 K, the film resistance decreases with increasing oxygen exposure. Beyond the peak maximum of the first TPD peak, the film resistance curves cross over, and between 300 and 400 K the film resistances are higher than that of the clean film, with a trend towards increasing resistance as a function of oxygen exposure. At 425 K, coinciding with the peak maximum of the second TPD peak, the film resistances drop back to that of the clean film, tracking the clean film resistance into the high-temperature regime. These data show that the presence of oxygen species on the surface of platinum and titania is reflected in measurable changes in film resistance.

CONCLUSION

This study has demonstrated that the electrical conductance of thin, discontinuous Pt/TiO_x films responds with high sensitivity to oxygen, hydrogen and propylene, without giving rise to significant changes in the corresponding XPS spectra. Initially continuous platinum films on top of metallic titanium break up into discontinuous structures upon high-temperature treatment in oxygen, followed by hydrogen reduction and a final reoxidation step in oxygen. The XPS results indicate that the platinum surface remains in the zero-valent state, regardless of gas environment, while titanium reacts with oxygen to form TiO₂. High-temperature reduction in H₂ leads to the formation of small amounts of Ti³⁺.

Exposure of activated films to oxygen at 550 K or higher causes large increases in film resistance, which can be attributed to the filling of surface and subsurface oxygen vacancies in TiO_x . Hydrogen and propylene exposure at elevated temperatures causes the film resistance to decrease, most likely due to the formation of surface hydroxyl groups followed by the removal of lattice oxygen and the creation of vacancy defects. Thanks to the presence of four-point conductance probes on the surface of the film, changes in the film conductance can be correlated with changes in surface coverage, providing a link between TPD spectra and conductance data.

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