Thermal stability of Pt films on TiO$_2$(110): evidence for encapsulation

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Abstract

We have studied the thermal stability of ultrathin platinum films on a rutile TiO$_2$(110) surface, using low energy ion scattering (LEIS) and X-ray photoelectron spectroscopy (XPS). At room temperature, Pt grows in three-dimensional islands on the TiO$_2$ surface, with little indication of an interface reaction. Upon annealing to temperatures above 450 K in UHV, encapsulation of the Pt islands by Ti suboxides is observed; the rate of this process increases with annealing temperature and decreases with island thickness. The Ti layer on top of the Pt islands is identified as a reduced Ti$^n^+$ species (1 $\leq n \leq$ 3) with the degree of reduction depending on the thickness of the Pt islands. These results are discussed in the framework of the strong metal–support interaction (SMSI) effect.

Keywords: Low energy ion scattering (LEIS); Metallic films; Metal–insulator interfaces; Platinum; Titanium oxide; X-ray photoelectron spectroscopy

1. Introduction

The Pt/TiO$_2$ system has been known for many years to exhibit unusual surface properties [1]. Platinum deposited as small particles onto the oxide readily adsorbs gases such as carbon monoxide or hydrogen. However these chemisorption properties are almost completely suppressed after reduction at high temperature. This behavior has been attributed to strong metal–support interactions (SMSI) [1]. The origin of this effect remains a subject of controversy [2]. Different mechanisms for the suppression of catalytic properties of Pt crystallites supported on TiO$_2$ have been proposed: The two main mechanisms involve either charge transfer, or encapsulation (the so-called ‘‘decoration model’’) [2]. Recently, the latter mechanism has received more attention. In this report, we provide further experimental evidence for an encapsulation effect in the Pt/TiO$_2$(110) system.

This study has been carried out in the framework of a systematic study of the growth of transition metals on TiO$_2$(110). The objective is to study the initial growth modes of transition metals on this insulator, and the thermal stability of the layers. The systematics began with chromium, iron and copper, in the 3d row. Different behavior is observed, de-
depending on the reactivity of the metal. In general, the more reactive the metal is towards oxygen, the more two-dimensional is the initial growth [3–6]. The study of additional metal overlayers (hafnium [6] and palladium [7]) have confirmed these trends: Hf is very reactive, and grows in almost flat 2D islands, while the behavior of Pd lies between those of Fe and Cu [7].

Iron [8] and palladium [7] films on TiO$_2$(110) have been reported to exhibit a property of interest for the present report, that is, an encapsulation behavior when as-deposited islands are heated in UHV. In order to study in some detail the characteristics of this phenomenon in the early stage of the growth of metals on TiO$_2$, we next chose platinum, a metal that is catalytically active, but which is not very reactive towards oxygen. In fact, platinum on TiO$_2$ is known to be a model system for studying strong metal–support interactions.

Previous studies using similar techniques have mainly focused on the catalytic properties of dispersed Pt on titania, and interest has been centered on the suppression of chemisorption capabilities [2,9]. Various TiO$_2$ supports have been used, and the presence of a reducing atmosphere has been necessary during annealing to produce the SMSI effect. In microscopic investigations [10,11] and spectroscopic studies (in particular LEIS [9,12], and XPS [13,14]) evidence for the encapsulation of Pt clusters on TiO$_2$ has been reported.

We have studied the thermal behavior of Pt on a TiO$_2$(110) single crystal in connection with a systematic study of the growth mode at the early stages [15]. As a model substrate, titania can be prepared with a well characterized stoichiometric (110) surface, and this makes it possible to investigate the fundamental mechanisms governing the interaction of the adsorbed metal with its oxide support. We are able to produce SMSI behavior in a UHV environment, without need of a reducing atmosphere of hydrogen.

The structure of this report is as follows: Section 2 gives a brief presentation of the experimental techniques used; Section 3 describes our LEIS and XPS data; a discussion of these results in the framework of the SMSI effect is presented in Section 4; finally, Section 5 summarizes the conclusions drawn from our study.

2. Experimental

The experiments have been carried out in a UHV system with a base pressure of $\sim 1.3 \times 10^{-10}$ Torr, which has been described elsewhere [16]. An X-ray source (Al K$_\alpha$, Mg K$_\alpha$) and a concentric hemispherical analyzer (100 mm radius) are used for X-ray photoelectron spectroscopy (XPS); a quadrupole mass spectrometer allows residual gas analysis; a retarding field display optics and an electron gun are used for low-energy electron diffraction (LEED); a differentially pumped ion gun is used for sputtering, and, in combination with the hemispherical energy analyzer, for low-energy ion scattering (LEIS) experiments. The latter are performed at a fixed scattering angle of 135°, using 1 keV $^3$He$^+$ ions at an ion fluence per measurement lower than $10^{14}$ ions/cm$^2$.

The sample, a TiO$_2$ single crystal with (110) orientation, is mounted on a X/Y/Z manipulator. It can be heated by means of radiation or electron bombardment, using a resistively heated W filament mounted behind the sample. For temperatures of 650 K and below, we use infra-red radiation; to anneal at temperatures greater than 650 K, we combine the radiative heating with electron bombardment, biasing the sample to a +300 V potential. The crystal temperature is measured using a tungsten/rhenium thermocouple spotwelded onto the Ta frame that holds the sample. The sample is cleaned by Ar$^+$ bombardment, followed by annealing in vacuum and in oxygen to restore the surface stoichiometry [17]. The Pt films are deposited using a shielded liquid-nitrogen-cooled metal source, through thermal evaporation from a small (2 mm $\times$ 2 mm) Pt foil spotwelded to a tungsten filament, at deposition rates of $\sim 0.5$ Å/min. During evaporation the pressure in the chamber may increase by 0.5 to 3 $\times$ 10$^{-10}$ Torr; this can lead to small contamination of the deposited layers for the longest evaporation times, characterized by a small (a few percent) underestimation of the Pt LEIS signal. The sample temperature remains unchanged to within $\pm 3$ K. The average layer thickness is monitored using a quartz crystal monitor (QCM). The thicknesses given in this article are average thicknesses, calculated by assuming uniformly thick films with the Pt bulk density, 21.4 g/cm$^3$. This gives an average distance between lay-
ers of about 2.5 Å, a value slightly greater than the distance between close packed (111) planes, 2.26 Å [18]. The latter will be taken hereafter as the average thickness of one "atomic monolayer".

3. Results

3.1. Growth mode of Pt on TiO$_2$(110)

We have investigated the early stage of the growth of platinum on TiO$_2$(110). Since the present study is devoted primarily to the thermal stability of the ultrathin Pt films on titania, we leave the presentation of the complete data for a separate report [15], and we present only the main results in Figs. 1a–1c. These depict the evolution of the LEIS contributions of Pt, Ti, and O, respectively, as functions of the average Pt thickness. The LEIS technique is sensitive mainly to the topmost layer at the surface [19], which allows us to detect the presence of adatoms at the early stage of the deposition, and to measure the disappearance of the substrate atoms for overlayer coverages greater than a threshold thickness. The result shows that the overlayer fully covers the substrate only after deposition of about 20 Å of Pt, a thickness at which the contributions from the oxide support (Ti, O) vanish (Figs. 1b and 1c). A fraction of the substrate atoms are still visible far beyond the average coverage of one atomic monolayer (around 2.5 Å). The behavior expected if growth were two-dimensional is indicated by dashed lines on Fig. 1. On the contrary, the observed behavior is clearly three-dimensional: Pt grows in the island mode on TiO$_2$(110). For Pt coverages greater than that necessary to suppress completely the LEIS Ti and O signals (i.e., about 20 Å), the Pt intensity reaches a plateau (Fig. 1a). Furthermore, little interface reactivity is observed, as indicated by the Ti 2p and Pt 4f XPS doublets, whose shapes show little alteration upon deposition [15].

3.2. Annealing the Pt films in UHV

We consider now the behavior of the platinum islands when the system is heated. Figs. 2a and 2b show a series of LEIS spectra measured for two platinum films on titania, 2.8 Å Pt annealed at 650
The annealing experiments are performed as follows. First, the film is evaporated in UHV onto the TiO₂ sample at room temperature. Then XPS and LEIS measurements are carried out. Second, the sample is heated for a limited time. XPS and LEIS measurements are then performed at room temperature. Third, a new annealing period follows at the

K, and 8.8 Å annealed at 800 K. Data for the stoichiometric surface, presented in the bottom curves of Fig. 2, display characteristic peaks at 760 and 420 eV that are attributed to the Ti and O atoms in the top surface layer. The peak at 980 eV is assigned to the Pt atoms adsorbed onto the TiO₂(110) surface. The curves show evidence for the disappearance of platinum from the topmost layer of the surface as the annealing time is increased, from top to bottom.

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![Fig. 2. Evolution of LEIS spectra as a function of cumulative annealing time, for 1 keV incident He⁺ ions. (a) 2.8 Å layer, annealed at 650 K for 0 (as deposited), 3, 8 15, 30 and 60 min (top to bottom); the spectrum of the stoichiometric surface is shown in bottom. (b) 8.8 Å layer annealed at 800 K for 0, 3, 8, 15 and 30 min, and stoichiometric. Notice the vanishing of the Pt signal, and the recovery of Ti and O peaks, for long enough annealing time.](image)

![Fig. 3. Evolution of the Pt LEIS intensity as a function of cumulative annealing time, for 2.8, 8.8 and 37.8 Å thick Pt layers, at: (a) 500 K; (b) 650 K; and (c) 800 K. Intensities are normalized to the "as-deposited" value.](image)
same temperature as before, followed by a new series of measurements, and so on. The annealing time given in the following, called hereafter "cumulative time", is calculated by adding the individual periods of successive annealing steps. The precision of the temperature measurement is estimated to be ± 30 K, but the thermal stability during the heating is estimated to be better than ± 3 K. Heating by radiation is used to minimize defect production by electron bombardment during the annealing procedure.

Before starting the annealing at 500 K for the 2.8 Å layer, the as-deposited spectrum exhibits a large platinum peak, together with oxygen and titanium peaks (top curve of Fig. 2a). After only 3 min at 650 K, the platinum peak is strongly attenuated, and after one hour, the peak has vanished, within experimental error (Fig. 2a). Correspondingly, the oxygen and titanium peaks have almost recovered their stoichiometric values (bottom spectrum). For the 8.8 Å layer, the as-deposited Ti and O LEIS peaks are barely visible after deposition, compared to the large Pt peak (top of Fig. 2b). The Pt contribution disappears after only 30 min at 800 K for this thickness. Correspondingly, the Ti and O contributions strongly increase.

The disappearance of the Pt signal depends on both coverage and temperature, as displayed in Figs. 3a–3c, where the Pt LEIS peak is plotted as a function of the annealing time. The annealing temperatures are 500 (Fig. 3a), 650 (Fig. 3b), and 800 K (Fig. 3c), and the average thicknesses are represented by black squares (2.8 Å), open triangles (8.8 Å), and filled circles (37.8 Å). At a given temperature, the Pt signal decreases faster for the thinner layers. For equivalent films, the Pt signal decreases faster at higher temperature. In the case of the 8.8 Å layer, for example, 120 min of annealing are not enough to suppress the Pt contribution at 650 K, but at 800 K, the Pt signal reaches zero after only 30 min. Surprisingly, the attenuation is significant even for a fairly thick layer of 37.8 Å; a 20% decrease is produced after 120 min at 800 K.

Our results show evidence of encapsulation at temperatures as low as 450 K, which seems to be a threshold temperature, not only for the decrease of Pt LEIS signal, but also for the appearance of a reduced Ti species, as we will see in Section 3.4 below.

3.3. Encapsulation of Pt islands

While platinum vanishes from the topmost layer during the annealing sequences described above, it must be pointed out that there is good evidence that the platinum islands are still present. For example, the XPS Pt 4f measurements presented in Fig. 4, for a 8.8 Å layer, show a moderate decrease in amplitude when the sample is annealed at 800 K (bottom curve), by comparison with the as-deposited spectrum (top curve). This can be interpreted as a masking of the emitted photoelectrons from Pt atoms, by some overlayer covering the Pt islands. We note that the annealing temperature is significantly below the Pt desorption temperature (for Pt to desorb in two hours of annealing, a temperature of 1500 K would be required, assuming that evaporation of Pt atoms from clusters is not very different from evaporation from bulk Pt). As a consequence, we can rule out desorption of Pt adatoms. The annealed curve (Fig. 4) also shows a shift of the Pt 4f binding energy in the direction of higher energies, by about 0.5 eV. The absence of significant change in the Pt 4f line shape is an indication that there is no or little interdiffusion at the surface. A small narrowing of the Pt 4f line width is also observed after annealing (Fig. 4), a behavior similar to that reported in the case of encapsulation of Fe islands on TiO₂ [8].

The overlayer can be removed by sputtering the sample with 1 keV Ne⁺ ions, as depicted in Fig. 5.

![Fig. 4. XPS Pt 4f doublet, plotted as a function of binding energy, for a 8.8 Å Pt layer. Top spectrum: as-deposited situation (Pt evaporation with sample at room temperature). Lower spectrum: layer heated at 800 K for 3 min (grazing emission).](image-url)
The LEIS Pt signal is close to zero after annealing the 7.1 Å layer at 800 K for 30 min. When the sample is exposed to a continuous flux of Ne⁺ ions, the Pt signal immediately reappears at low fluence. We interpret this to mean that the overlayer is sputtered off the islands, uncovering them. The Pt signal rises, passes through a maximum, and then decreases as Pt is slowly sputtered itself. The Pt overlayer is easily removed, indicating an overlayer thickness not much more than a few atomic layers.

Our physical interpretation of the disappearance of platinum from the topmost layer during the annealing sequence of Fig. 3 lies in the encapsulation of Pt islands. As the temperature is raised above 450 K for a long enough time in UHV, the platinum islands are covered by an overlayer, as depicted in Fig. 6. Only Ti and O are present (as attested by LEIS and XPS), and no other element is added, since annealing is performed in UHV. So this layer must be made of some titanium suboxide, TiOₓ.

3.4. Study of the suboxide overlayer

The chemical nature of the new layer that encapsulates the Pt clusters can be partly deduced from Figs. 7−9, which display a series of Ti 2p XPS spectra for various Pt thicknesses and different annealing temperatures. Curves of Figs. 7a, 8a and 9a were obtained for a close-to-normal emission angle, 10° off-normal. Curves of Figs. 7b, 8b and 9b were obtained for a grazing emission angle, 70° off-normal. Since the escape length of 460 eV Ti 2p electrons is of the order of 10 Å, the substrate contribution dominates for photoelectrons emitted close to the sample normal, whereas the contribution from photoelectrons emitted close to the topmost atomic layers dominates for grazing emission; the grazing emission is more "surface-sensitive".

Each of the Figs. 7−9 show the as-deposited condition in the bottom spectra; upper curves correspond to the annealed surface, with annealing time increasing from bottom to top. Pt thicknesses and
annealing temperatures are: 2.8 Å at 500 K for Fig. 7, 8.8 Å at 800 K for Fig. 8, and 37.8 Å at 800 K for Fig. 9, respectively. In each case, the Ti 2p doublet associated with the as-deposited layer is characteristic of the stoichiometric surface, in binding energy as well as in shape, and corresponds to the Ti$^{4+}$ oxidation state. As the support is covered by Pt islands, a decrease of Ti 2p intensity occurs as Pt coverage increases, reflecting the loss in free TiO$_2$ surface (see also LEIS curves of Figs. 1b and 1c).

The XPS Ti 2p signal resulting from photoelectrons emitted close to the normal shows some evidence of reactivity upon annealing at temperatures as low as 500 K. For instance, at 500 K, the arrow in Fig. 7a indicates the existence of a very small tail on the low-binding energy tail of the 2p$_{3/2}$ line. In contrast to the close-to-normal situation, the grazing-angle curves of Fig. 7b exhibit a clearly visible shoulder in the same energy range. This shoulder is attributed to the presence of Ti atoms with oxidation states different from stoichiometric TiO$_2$:Ti$^{n+}$ species appear (with $0 \leq n < 4$), in addition to the Ti$^{4+}$ species. This means that charge transfer takes place in the overlayer, and that titanium cations are reduced.

However, part of this reduction process may be attributed to the evolution of the heated TiO$_2$ surface alone. We have examined the effect of annealing the uncovered surface of stoichiometric TiO$_2$(110) under UHV conditions [20]. We find that reduction of a low concentration of surface Ti occurs after annealing at moderate temperatures, i.e., even for $T < 500$ K a small but measurable Ti$^{3+}$ state can be observed in the Ti 2p curves; moreover, XPS measurements at grazing angle indicate that this Ti$^{3+}$ species is lo-
cated near the surface region [20]. Such a production of Ti$^{3+}$ sites after annealing stoichiometric TiO$_2$ has recently been reported [21]. This means that not all of the low-energy tail of Figs. 7 may be attributed to the migrating suboxide, but may also contain contributions from the uncovered TiO$_2$ surface. Nevertheless, the LEIS data of Figs. 3 and 5 clearly demonstrate that encapsulation occurs, regardless of the existence of substrate reduction.

The spectra of the annealed layers can be interpreted as the superposition of a stoichiometric contribution, due to the support, and of a suboxide contribution, due to the overlayer. This assumption is backed by the fact that the reduced-to-stoichiometric amplitude ratio increases for grazing emission. This means that most of the reduced species are located in the near-surface region, since the grazing emission XPS is more “surface-sensitive”. However, there may also be reduced species at the interface between Pt and substrate.

The reduction process is enhanced as the temperature is increased (Fig. 8): the contribution of the reduced species becomes even larger than the stoichiometric one, as the Pt thickness is increased. The degree of reduction depends on the thickness of the Pt islands. For the thickest layer (37.8 Å, Fig. 9), the reduced species dominate the Ti 2p emission, especially for grazing-angle emission. The reduced state can be interpreted as a Ti$^{n+}$ state with $n < 2$. The core-level shift is large; about 4 eV. The suboxide TiO$_x$ has an $x < 1$. There does not appear to be evidence for metallic Ti (the expected core-level shift for elemental Ti ranges beyond 5 eV [22]).

Deconvolution of the XPS Ti spectra of Fig. 7 (not shown) indicates that the stoichiometric contribution (Ti$^{4+}$) changes by less than 30% after the complete thermal treatment. Thus the fraction of the uncovered TiO$_2$ surface is not significantly different after annealing. At the same time, the Pt 4f amplitude changes little (Fig. 4), so we conclude that the Pt island size changes little through this process.

Fig. 10 displays the LEIS Ti intensity as function of annealing temperature, for three different Pt thicknesses, 5.1 Å (filled circles), 8.9 Å (open squares), and 18.9 Å (filled diamonds). The layer has been deposited at room temperature. The sample has then been annealed at each (increasing) temperature for 15 min, and then cooled down at room temperature for LEIS measurements. For a given thickness, the Ti intensity increases as temperature increases. This reflects the fact that encapsulation is thermally activated. At high enough temperature, the Ti intensity reaches even higher values than for stoichiometric TiO$_2$, e.g., 1.8 times higher for the 18.9 Å layer at 900 K. This indicates that the overlayer consists of a suboxide TiO$_x$ with a higher Ti concentration than in TiO$_2$. This is consistent with XPS results, which indicate that $x$ can be lower than 1. For example, Fig. 11 displays the Ti 2p doublet after long annealing times, for grazing emission. From top to bottom,
thickness is increased from 0 (stoichiometric) to 2.8 Å at 650 K for 60 min, 8.8 Å at 650 K for 120 min, and to 37.8 Å at 800 K for 120 min. This figure allows us to compare quantitatively the behavior displayed in Figs. 7–9, in a single plot at the same scale. The stoichiometric contribution steadily decreases as the support is covered by Pt islands, the contribution of the overlayer becomes predominant, and the Ti is more and more reduced (arrows).

Fig. 12 displays more quantitatively the evolution of integrated XPS Pt 4f (Fig. 12a) and Ti 2p (Fig. 12b) intensities as functions of the annealing time, for both close-to-normal (filled triangles), and grazing (open squares) emission angles, and for a 2.8 Å layer annealed at 650 K. The close-to-normal curves (solid triangle) show little variation of intensity, especially as far as Pt and O (not shown) are concerned; the Ti intensity variation amounts to about 8%. This indicates little change in the sizes or shapes of the Pt islands on the oxide substrate. However the situation is different for grazing emission, which is more surface-sensitive. We observe a decrease of 25% for Pt 4f amplitude, and an increase of 30% for Ti 2p. This reflects the occurrence of the new contribution from the encapsulating overlayer, superimposed on the substrate contribution.

3.5. Stability of encapsulated layers and influence of substrate preparation

Encapsulation of Pt islands by a TiO$_x$ suboxide has been reported to be reversible. For example, using LEIS measurements somewhat similar to ours, Dwyer et al. observed the reappearance of the Pt LEIS peak after a thermal treatment in the presence of oxygen [9]. They heated a 10 Å layer at 875 K in 10$^{-6}$ Torr of O$_2$. They observed a partial reappearance of the Pt LEIS signal after 20 min, and a complete recovery after 40 min. In contrast to this behavior, we were not able to detect evidence for uncovering the Pt islands after annealing the sample in oxygen (up to 1000 K in 10$^{-6}$ Torr). De-encapsulation does not appear to occur under our conditions. On the contrary, a new layer with TiO$_2$ stoichiometry is formed on top of the Pt islands (not shown). To account for this difference, it is possible that the details of the annealing process as well as sample preparation might have some influence on this phenomenon.

Encapsulation also occurs for a heavily Ar$^+$-sputtered surface (not shown). This indicates that encapsulation is not sensitive to the presence of defects such as oxygen vacancies. The phenomenon does not seem to involve the migration of Ti atoms only: our LEIS measurements for a relatively thick layer show that oxygen also reappears on the topmost layers upon annealing. However the XPS curves of Figs. 7–9 show that the Ti atoms feel a more highly reduced environment as they migrate on thicker and thicker Pt islands, indicating that the
Ti/O ratio increases. In the case of the 37.8 Å layer, the Ti 2p line is shifted by almost 4 eV relative to the stoichiometric TiO₂ surface. This binding energy is consistent with an oxidation state of Ti⁴⁺, which corresponds to TiO. However, due to the width of the Ti 2p XPS peaks, the coexistence of more reduced forms of Ti cannot be ruled out [22]. At lower thickness, the XPS curves probably result from a distribution of Tiⁿ⁺ species, with the average n closer to 3.

The results are thus consistent with a migration of Ti and O atoms from the support and the formation of a TiOₓ suboxide on top of the Pt islands. The islands are covered completely after annealing in UHV at high enough temperature for a long enough time.

4. Discussion

4.1. Strong metal–support interaction

We can discuss the encapsulation process within the context of the so-called strong metal–support interactions (SMSI) effect. Encapsulation is believed to explain the suppression of chemisorption properties on metallic particles, when the reducible titanium oxide support is annealed in a reducing atmosphere, such as hydrogen. Tauster and co-workers coined the acronym SMSI to interpret the modification of catalytic properties in terms of chemical reactivity between the oxide and the supported noble metal. However they emphasized the role of chemical bonding between the metal and the support, ruling out a possible encapsulation [1].

Later investigators have since proposed two kinds of models to take into account the SMSI behavior, both describing a part of the intricate phenomenon. On the one hand, the “decoration model” explains the loss of catalytic properties by a high-temperature reduction, causing a TiOₓ species to move over and partially cover the supported metal particles. The reversible migration of a TiOₓ suboxide would partly account for the disappearance and reappearance of chemisorption capabilities of the Pt crystallites [2,12,13]. This is the same as encapsulation. On the other hand, models oriented towards more chemical properties invoke charge-transfer effects to be responsible for the observed behavior [2]. Of course, both points of view describe a complementary part of the truth, since even if the blocking of chemisorption sites arises from a purely geometrical effect, it remains for us to understand the nature of the driving force for the migration of the Ti suboxide.

Direct observations of encapsulated Pt on TiO₂ by means of microscopic investigations have been reported for high area Pt/TiO₂ catalysts. Wang et al. have presented high resolution electron micrographs showing small Pt particles covered with a Ti suboxide after heating in H₂ atmosphere [10]. They find that the higher the reduction temperature, the less mobile the oxide layer becomes over the metal particle. This is contradictory to what we observe: Figs. 3a and 3b show that encapsulation is more complete as temperature is increased (from 500 to 800 K). Wang et al. also report the existence of Pt–Ti intermetallic compounds, such as PtTi or Pt₃Ti [10].

Later, Yao performed HREM experiments demonstrating the existence of crystalline TiOₓ overlayers, a few atomic monolayers thick, covering Pt islands on high-area TiO₂ powders [11]. He finds that TiOₓ overlayers are ordered on Pt(111); this indicates an epitaxial relationship. This seems to be in disagreement with what is suggested from field-emission microscopy results by Vanselow and Mundschau, who studied the migration of TiOₓ over a Pt tip: they find that the kinetics of diffusion do not favor covering Pt(111) by a monolayer, and that the oxide covers preferentially high Miller index planes; in particular, the (111) plane is resistant to covering by migration of TiOₓ [23]. One should however mention that the experimental situations in the two experiments were rather different. Our studies on the stoichiometric TiO₂(110) surface indicate the growth of Pt islands (111) orientation [15]. Migration (or diffusion) of Ti species is observed even at coverages, where the TiO₂ surface is completely covered with Pt, as exemplified in Figs. 9a and 9b for a 37.8 Å Pt layer. A small thickness of the TiOₓ overlayer is consistent with its rapid removing by Ne⁺-sputtering (Fig. 5).

Other groups reported the migration of titania species in the Pt/TiO₂ system, using Rutherford backscattering [24] or LEIS [9,12,25] techniques. The resulting encapsulation has been promoted in most of these studies by annealing TiO₂-supported Pt
crystallites in hydrogen. What is remarkable in the present case is that the annealing is sufficient to cause an SMSI behavior even in a UHV environment, that is, after annealing in the absence of a reducing atmosphere. Another indication of this striking property has been reported by Sadeghi and Henrich in the case of Rh/TiO$_2$ [26]. They proposed two explanations for this fact: either hydrogen is not necessary for the migration of Ti oxides onto the metal, or enough interstitial H atoms are present in TiO$_2$ under UHV conditions. More probably, we may invoke a simpler mechanism, as already noted in Section 3.4, involving the migration of a reduced Ti$^{3+}$ species on top of Pt islands. In effect, such a species is observed near the surface of stoichiometric TiO$_2$(110) upon annealing in vacuum at moderate temperatures (less than 500 K) [20,21]. The interaction of Ti$^{3+}$ with Pt atoms could be responsible for the energetically favorable configuration on top of the islands, rather than on the surface of TiO$_2$ or in the bulk.

For the sake of completeness, we note that encapsulation also occurs with substrates not as reducible as TiO$_2$, such as Pt/Al$_2$O$_3$. In this case, encapsulation is accompanied by interdiffusion (for fairly thick Pt films: 2000 Å) [24]. Metals on Nb$_2$O$_5$ (niobia) also exhibit the same migration properties as the Pt/TiO$_2$ system [2]. To some extent, V$_2$O$_3$ and CeO$_2$ oxides are also similar [2]. It must be pointed out that encapsulation does not occur for all oxides (e.g., SMSI effects have not been found with SiO$_2$), and that the SMSI effect is stronger for reducible oxides.

4.2. Comparison with encapsulation of Fe

It is useful to compare the present results with data for the growth and thermal stability of Fe on TiO$_2$(110). Pan et al. used the same experimental techniques as ours and found evidence for the migration of a titanium suboxide on top of Fe islands after annealing in UHV [8]. Encapsulation occurs for Fe only at temperatures greater than 800 K, while a temperature of 450 K is sufficient for us to detect the encapsulation of Pt islands. It can be noted that wetting of the substrate TiO$_2$ is better in the case of Fe, which grows as flatter islands than Pt. Also, Fe is more reactive towards oxygen than Pt. For instance, a chemical interaction of Fe with the substrate occurs, as deduced from a small reduction of Ti upon deposition [5], whereas the deposition of Pt on TiO$_2$ shows no evidence of reactivity [15]. This is not surprising, since wetting is also affected by interface reactivity, and is not a matter of surface tensions only. In the case of encapsulation, we also note that the surface energy of the TiO$_2$ suboxide is not necessarily identical to that of TiO$_2$.

The XPS signal from the reduced species is proportionally larger for Pt than for Fe, which may indicate a thicker overlayer, or a different stoichiometry (i.e., a TiO$_x$ suboxide with a smaller x in the case of Pt). In support of this assumption, note on Fig. 10 that the Ti LEIS annealed/stoichiometric ratio reaches a value greater than 1 beyond 700 K. This means that the Ti suboxide covering the islands becomes richer in Ti than TiO$_2$, as the annealing temperature is increased. At the same time, the oxygen signal does not rise as much. This situation is opposite to the case of Fe, where oxygen is more abundant [8].

Another observation with Pt/TiO$_2$ can be paralleled with the Fe/TiO$_2$ system: after encapsulation takes place, the Fe 2p and Pt 4f XPS lines are narrower than in the as-deposited case (Fig. 4 and Ref. [8]; see Section 3.3). This sharpening is consistent with all of the Pt atoms in clusters being in a more three-dimensional environment: The coordination of Pt surface atoms increases at the encapsulated interface, and there is a partial recovery of a more bulk-like coordination number. In this interpretation, the 0.5 eV shift of the 4f lines to higher binding energy (Fig. 4), could be interpreted as a surface core-level shift. Note that the Fe 2p core-level shift is in the opposite direction upon encapsulation of Fe/TiO$_2$ [8]. Note also that a shift in the direction of smaller energy is observed during the growth of Pt on TiO$_2$(110) at low coverage [15]. The latter shift has been attributed to different final state screenings for Pt in metallic clusters, and for Pt in contact mainly with TiO$_2$ [15]. On the other hand, we would not attribute the shift of Fig. 4 to such a final-state effect, but rather to an initial-state effect due to a more three-dimensional environment for Pt atoms in encapsulated islands. The latter effect is expected to give a shift towards larger binding energy, as observed.
4.3. What is the driving force for the encapsulation?

Encapsulation has been observed for several metal overlayers on TiO$_2$: iron [8], palladium [7], rhodium [26], and platinum (this work, and Refs. [9–13]). These elements are located on the right side of the transition metal series. Encapsulation has not been observed on TiO$_2$ for more reactive elements, such as chromium [3] and hafnium [6], or titanium itself, on the left side of the series. On the other hand, these elements display a better wetting ability [3].

Bearing in mind that the encapsulation phenomenon is dependent on the element, it is nevertheless worthwhile trying to draw some general characteristics from the reported features. Encapsulation may be paralleled with wetting properties, considering the balance of surface energies: if element A wets element B, B does not wet A (when the interfacial energy plays no significant role). As a consequence, when good wetting is observed, encapsulation should be less favored, while when bad wetting is observed, the conditions may be favorable for encapsulation. In the Pt/TiO$_2$ case, Pt would play the role of element B, not wetting the titanium dioxide, and the TiO$_x$ suboxide would play the role of element A (of course this crude scheme assumes that TiO$_2$ and TiO$_x$ have similar surface energies).

This argument can be developed slightly further by remarking that if the metal–metal interaction is stronger than the metal–oxide interaction, then the mobility of metal atoms is enhanced, so the wetting ability is expected to be reduced. Moreover, if the metal–oxide interaction is stronger than the metal–metal interaction, then the formation of an oxide (a MeO$_y$ species) is possible. The latter would compete with the migrating TiO$_x$ suboxide, preventing the encapsulation of the metal crystallites, since the migration of oxygen would be favored rather than the migration of titanium. These effects may also compete with the metal forming a ternary oxide with TiO$_2$.

This reactivity argument is consistent with the observed situation, as far as the wetting properties are concerned, and encapsulation as well. Thus, Cr and Hf, two reactive metals, exhibit good wetting properties on TiO$_2$(110), but no encapsulation takes place. Elements such as Fe, Pd and Pt wet titania poorly, but encapsulation occurs.

The situation of Fe and Pt can be paralleled in the light of their respective reactivities. First, we note that the initial growth mode of Fe on TiO$_2$ is three-dimensional, with Fe forming flat islands [3]. The growth of Pt is also 3D, but with thicker islands [15]. Second, oxidation of ~0.5 ML of Fe occurs on deposition in UHV at room temperature, which can be interpreted as due to a larger reactivity towards oxygen. On the other hand, Pt exhibits no indication of interface reaction on deposition. Third, complete encapsulation of islands take place in both cases, but the chemical nature of the TiO$_x$ suboxide is different: the reduction of Ti on annealing in UHV is much more extensive for Pt (Ref. [8] and Figs. 7–9) than for Fe, indicating stronger Pt–Ti bonds than Pt–O, leading to a smaller x. Roughly, we can state a condition for encapsulation this way: the less reactive the deposited metal towards the oxide, the less effective the wetting, and the more reduced the suboxide migrating on the top of the islands.

Within this interpretation, the driving force for encapsulation would be the balance between metal–oxide and metal–metal interactions, which also accounts for the wetting properties. Of course, such a scheme can only be a zero-order mechanism, since the interface energy of the metal–oxide junction must also be taken into account, as well as kinetic considerations due to diffusion barriers for the migration of Ti and O atoms on the top of Pt islands. Furthermore, it is beyond the scope of this study to correlate the encapsulation behavior to the changes induced on the chemisorption properties.

However, this scheme fails to account for the Au/TiO$_2$ system [20]. Gold is located next to Pt in the periodic table, and might be expected to exhibit properties similar to Pt. Like Pt, Au forms clusters upon deposition on TiO$_2$ and shows very little evidence of reactivity. Although Au exhibits very poor wetting properties on TiO$_2$(110), it still displays a complete absence of encapsulation upon annealing in UHV [20]. This suggests that other parameters are necessary in order to describe the encapsulation phenomenon satisfactorily. For instance, in order for encapsulation to occur, perhaps the metal must be sufficiently reactive to catalyze decomposition of TiO$_2$ to TiO$_x$ + O$_{2-x}$, but not so reactive that a bulk oxide (binary or ternary) will form. In this respect, gold does not appear to be reactive enough to pro-
mote the decomposition or migration of a titanium suboxide.

5. Summary

We have observed the encapsulation of ultrathin platinum films vapor-deposited onto a TiO$_2$ single crystal with (110) orientation. Platinum forms islands in the early stages of its three-dimensional growth on titania. Using low-energy ion scattering, we observe the disappearance of Pt from the topmost layer of the surface, as the crystal is heated in ultrahigh vacuum above 450 K. Correspondingly, LEIS data show that only Ti and O atoms are present at the surface, indicating that a TiO$_x$ suboxide migrates on top of the Pt layers. Our data also indicate that the Pt island sizes do not change significantly during this process, and that the overlayer is only a few monolayers thick. Our XPS measurements of the Ti 2p line show that the $x$ value decreases as the Pt thickness is increased.

Our results suggest that encapsulation occurs at a lower temperature than previously expected, and that the migration process takes place even in absence of a reducing atmosphere. We did not observe a reversal of the process by annealing the encapsulated islands in the presence of oxygen.

Encapsulation occurs with TiO$_2$ for materials that show a low tendency towards wetting, such as Fe, Pd or Pt, and is not observed for more reactive elements, such as Cr or Hf. We suggest that simple energetic considerations provide hints for understanding the driving force of this phenomenon. However, more detailed models are required to account for the behavior of noble metals.

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