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# SINGLE CRYSTAL MODELLING OF THE SMSI PHENOMENON: STRUCTURE, COMPOSITION, ELECTRONIC EFFECTS AND CO CHEMISORPTION AT THE Ru(0001)/$TiO_x$ INTERFACE

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LEED, CO chemisorption, Auger and XP spectroscopy have been used to investigate the growth morphology, structure, kinetic behaviour and chemical properties of $TiO_x$ films on Ru(0001) as a function of oxide loading and temperature. The system exhibits a number of interesting properties which are of direct relevance to the SMSI phenomenon; these properties are critically dependent on the method of preparation.

## 1. Introduction

Single crystal model systems can provide a useful means of probing both reaction mechanisms and surface phenomena which are fundamental to heterogeneously catalysed processes. This approach may be used to investigate aspects of metal/support interactions by adopting a procedure in which thin films of support material are deposited on a single crystal substrate of the relevant metal [1–3]. It represents a particularly attractive strategy in the case of systems which are capable of exhibiting the phenomenon of Strong Metal Support Interaction (SMSI). A number of explanations have been advanced to explain SMSI behaviour, including migration of partially reduced oxide support species across or through the metal particles [4–7] or the formation of alloys between the metal and support species [8–13]. In the former case the chemical identity (electronic state) of the supposed migrating species is of considerable interest; in the latter case, the constituent elements of the supported alloy phase are open to question.

In this article we summarise results obtained by LEED, Auger spectroscopy, XPS and temperature programmed desorption which addresses some basic issues of relevance to SMSI in the Ru/$TiO_x$ system. The objects are to demonstrate convincingly that the model system can be set up reliably and reproducibly in

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both non-SMSI and SMSI conditions; to characterise any differences in structure, composition or electronic properties between the two cases, and to correlate these with the CO chemisorptive properties of the system. A principal aim is to assess the relative importance to the surface chemistry of site-blocking effects due to titanium oxide species and more subtle effects due to changes in electronic structure and composition. The use of a single crystal specimen avoids problems associated with other types of macroscopic specimens (e.g. polycrystalline foils) where diffusion of species such as TiO$_x$ along grain boundaries is energetically more favourable than surface to bulk transport [14]. Among other things, one should be able to establish whether the postulated diffusion of TiO$_x$ into the bulk structure of Group VIII metals [15] actually can occur at temperatures pertinent to the induction of SMSI behaviour.

## 2. Experimental

A description of the apparatus and the methods of specimen preparation and cleaning has been published elsewhere [16]. Deposition of titanium oxide on the single crystal Ru(0001) specimen was carried out by controlled evaporation of Ti from a collimated Ti evaporation source in an ambient atmosphere of oxygen at a pressure of $1 \times 10^{-6}$ torr. We have shown elsewhere [17] that this results in laying down of an ultra thin TiO$_x$ film whose 'as-deposited' stoichiometry corresponds to $x = 2$ at monolayer completion. After this treatment the specimen surface consists of regions of Ru which are covered by the TiO$_x$ film and regions of Ru covered by chemisorbed oxygen. A crucial consideration, therefore, is selective removal of the chemisorbed oxygen without significant perturbation of the TiO$_x$ films. This can present major difficulties when attempting to model metal/TiO$_x$ systems by this general approach [19,20]. We have demonstrated that selective removal of chemisorbed oxygen can be achieved by holding the specimen at 573 K and irradiating it with the flux of hydrogen atoms and ions issuing from a hot cathode low energy ion source [17]. By this means it is possible to generate in a controlled and reproducible way the initial surface condition required for chemical experiments: patches of TiO$_x$ film on an otherwise clean, bare Ru substrate.

In the results which follow (except section 3.1) each experiment was carried out by depositing a fresh dose of TiO$_x$ followed by removal of ruthenium-chemisorbed oxygen, as described above. After each observation, surface TiO$_x$ was removed by Ar$^+$ etching (300 K, 600 eV, $10^{-4}$ A/m). In those cases where measurements resulted in significant solution of the TiO$_x$ phase into the bulk metal, it was removed by cycles of heating in oxygen (1250 K, $10^{-7}$ torr) and Ar$^+$ etching [16] followed by annealing at 1350 K in $10^{-7}$ torr oxygen. Traces of dissolved oxygen were then removed by rapid heating to 1550 K in ultra high vacuum [17].

## 3. Results and interpretation

### 3.1. GROWTH MODE OF TiO$_x$ ON Ru(0001)

Figure 1 shows the Auger electron signals due to Ru(231 eV), Ti(387 eV) and O(510 eV) as a function of titanium oxide deposition time with the specimen at 300 K in an oxygen pressure of $10^{-6}$ torr. Exposure of the specimen surface to the sampling electron beam was kept as low as possible in order to minimise electron beam effects on the TiO$_x$ film. It can be seen that breaks occur at regular intervals in all three sets of data, behaviour which is characteristic of monolayer-by-monolayer growth (Frank-van der Merwe mechanism [18]); the Ti/Ru intensity ratio at the first break point provides a calibration value for monolayer coverage by this 'as deposited' phase. At the point of monolayer coverage the system exhibited a weak (1 × 1) LEED pattern; this sharpened up significantly on annealing to 400 K, an effect which is known *not* to be due to agglomeration or dissolution of the TiO$_x$ deposit with concomitant exposure of bare Ru surface (see below). It therefore suggests that this mild thermal treatment results in the formation of a TiO$_x$ overlayer which is essentially in registry with the Ru(0001) plane.

### 3.2. TEMPERATURE DEPENDENT BEHAVIOUR OF TiO$_x$ FILMS ON Ru(0001)

*The manner in which the Ru/TiO$_x$ system evolves as a function of temperature is critically dependent on the initial TiO$_x$ loading.* Figure 2a illustrates the behaviour

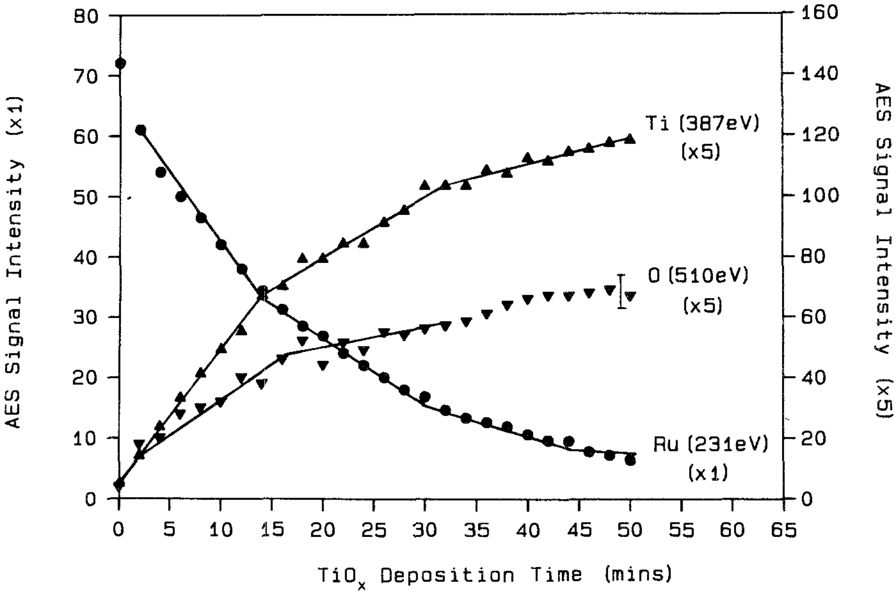

Fig. 1. Uptake of TiO$_x$ by Ru(0001) at 300 K monitored by Auger spectroscopy.

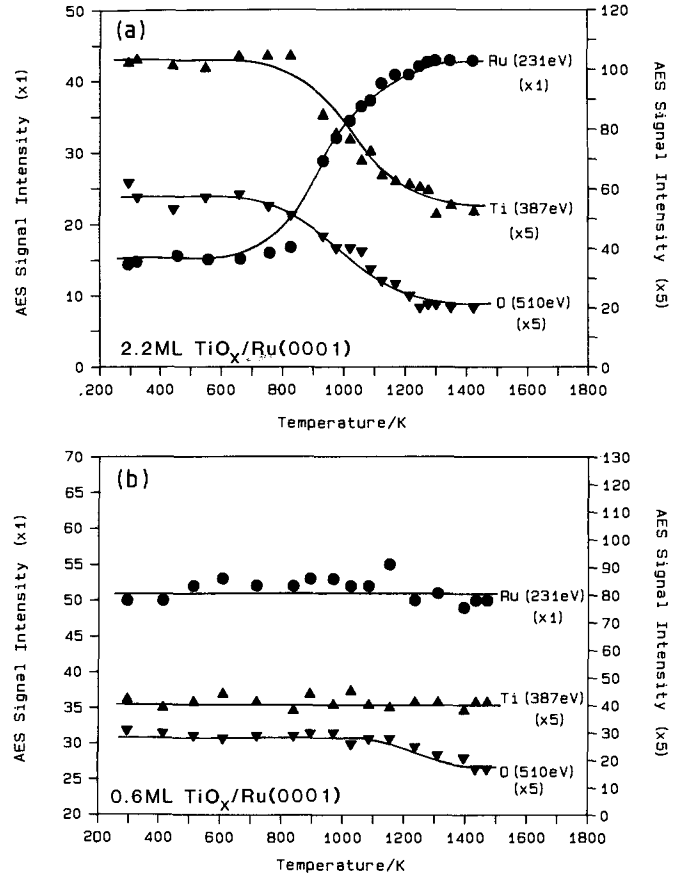

Fig. 2. (a) Showing temperature dependent behaviour of TiO$_x$ film an initial coverage *above* the critical value; initial loading 2.2 ML TiO$_x$. (b) Temperature dependent behaviour of TiO$_x$ film for an initial coverage *below* the critical value; initial loading 0.6 ML TiO$_x$.

of the system for an initial TiO$_x$ loading of 2.2 monolayers (ML). The data were obtained by heating the sample for fixed periods of time (60 s), the procedure being repeated with successively higher temperatures. (Control experiments showed that the quenching procedure did not affect any of the Auger intensities, so the results truly reflect the surface concentrations of species at the various temperatures). It can be seen that a regime of effectively constant composition up to ~ 800 K is followed by a temperature range in which very substantial decreases occur in the Ti and O signals accompanied by correspondingly large increases in the Ru signal. Finally, for temperatures > 1300 K the composition of the surface remains essentially constant again. These intensity variations are consistent with either agglomeration of the TiO$_x$ phase or its dissolution into the bulk of the Ru metal. The CO chemisorption results to be presented later effectively rule out the first of these possibilities; dissolution of TiO$_x$ in Ru must be occurring at temperatures > 800 K. Note that this is precisely in the range of temperature which is relevant for the onset of SMSI effects in the Ru/TiO$_x$ system. Based on the coverage calibration provided by fig. 1, the limiting high temperature Ti/Ru ratio in fig. 2(a) corresponds to a residual surface coverage 0.68 for the TiO$_x$ phase after annealing.

For *initial* TiO$_x$ loadings which correspond to $< 0.68$ ML the temperature dependent behaviour of the system is completely different. Figure 2(b) illustrates data for an initial TiO$_x$ loading of 0.6 ML. It is apparent that the Ti and Ru Auger signals are now essentially independent of temperature, while the oxygen signal exhibits a much smaller relative change than in the 0.68 ML case. It should be emphasised that this behaviour was consistent and reproducible: high temperature annealing of any initial TiO$_x$ loading greater than 0.68 ML always led to an eventual residual TiO$_x$ coverage of 0.68 ML; TiO$_x$ initial loadings *below* this critical value showed no significant variation in the Ti and Ru signals upon subsequent annealing.

### 3.3. LEED AND XPS RESULTS

The 0.68 ML TiO$_x$ surface phase described above gave rise to a characteristic LEED pattern which can be indexed in terms of a $(5\sqrt{3} \times 5\sqrt{3})$R30° unit mesh.

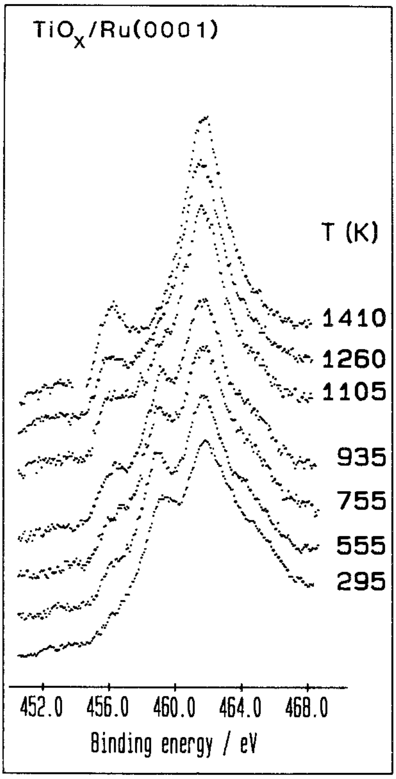

Fig. 3. XP spectra as a function of annealing temperature of the TiO$_x$ film. Note that the large feature around 462 eV is mainly due to the Ru(3p$_{3/2}$) level, with some contribution from Ti(2p$_{1/2}$). The feature which shifts from 459.2 eV to 456.0 eV is the Ti(2p$_{3/2}$) emission.

It is of considerable interest that the ratio of the unit mesh areas Ru(0001):

$(5\sqrt{3} \times 5\sqrt{3})R30° = 0.64:1$

observed by LEED bears a close numerical correspondence with the value of 0.68 ML determined by Auger spectroscopy as the critical initial loading for the formation of a stable or 'equilibrium' Ru/$TiO_x$ surface phase. This point will be returned to below. Annealing freshly deposited $TiO_x$/Ru(0001) overlayers resulted in substantial shifts in Ti core level binding energies (BEs) observed by XPS (fig. 3). For the 'as-deposited' $TiO_x$ film the Ti($2p_{3/2}$) BE was 459.2 eV. This figure is consistent with our proposed model for the initial $TiO_x$/Ru film which may be thought of as based on NaCl-type (111) planes: Ru(0001) || O || Ti || O. Here, a monolayer sheet of $TiO_2$ lies on top of the Ru substrate, the presence of the Ru atoms causing the Ti atoms to carry a somewhat larger net positive charge than they do in bulk $TiO_2$ [17]. Annealing of the initial $TiO_x$ film ($x = 2$) leads to formation of the stable 'equilibrium' phase which exhibits a substantially greater Ti($2p_{3/2}$) BE of 456.0 eV. This 3.2 eV decrease in BE is consistent with the transformation $TiO_2 \rightarrow TiO$ [22] and, as will be shown, along with the Auger, LEED and CO chemisorption data provides the basis for a coherent picture of the Ru/$TiO_x$ interface.

### 3.4. CO CHEMISORPTION ON Ru(0001) IN THE PRESENCE OF NON-ANNEALED AND ANNEALED $TiO_x$ FILMS

The effect of $TiO_x$ deposition on the subsequent uptake of CO by Ru was investigated under two distinctly different sets of conditions: (i) in the presence of the 300 K "as deposited" $TiO_x$ film (i.e. non-SMSI condition) (ii) after pre-annealing the $TiO_x$ film to 1100 K for 4 minutes: conditions which are pertinent to the induction of SMSI behaviour. Figure 4(a) shows results for the temperature programmed desorption of CO from Ru(0001) following adsorption of a saturation gas dose (~ 50 Langmuir) at 300 K on to a surface loaded with varying amounts of *unannealed* $TiO_x$. The clean surface spectrum exhibits the two molecular CO peaks ($\beta_1$, $\beta_2$) characteristic of clean Ru(0001) [16]; these are progressively suppressed by the $TiO_x$ film, without the appearance of any new desorption features. It can be seen that the surface is effectively completely blocked to CO chemisorption at a $TiO_x$ loading close to 1.0 ML (recall that this latter quantity is calculated from the Auger spectra). Figure 4(b) shows the dependence of the integrated CO desorption yield on $TiO_x$ coverage: it appears that CO uptake depends linearly on $TiO_x$ precoverage right up to the cut-off value at 1.0 ML. This suggests that the as-deposited $TiO_x$ film produces a simple geometric site-blocking effect, without the involvement of any long range electronic effects on the metal surface. The latter conclusion is consistent with the observation that the CO peak temperatures are relatively unaffected by the presence of $TiO_x$ (the small downward shift of the $\beta_2$ peak may be due to the decreasing size of CO islands).

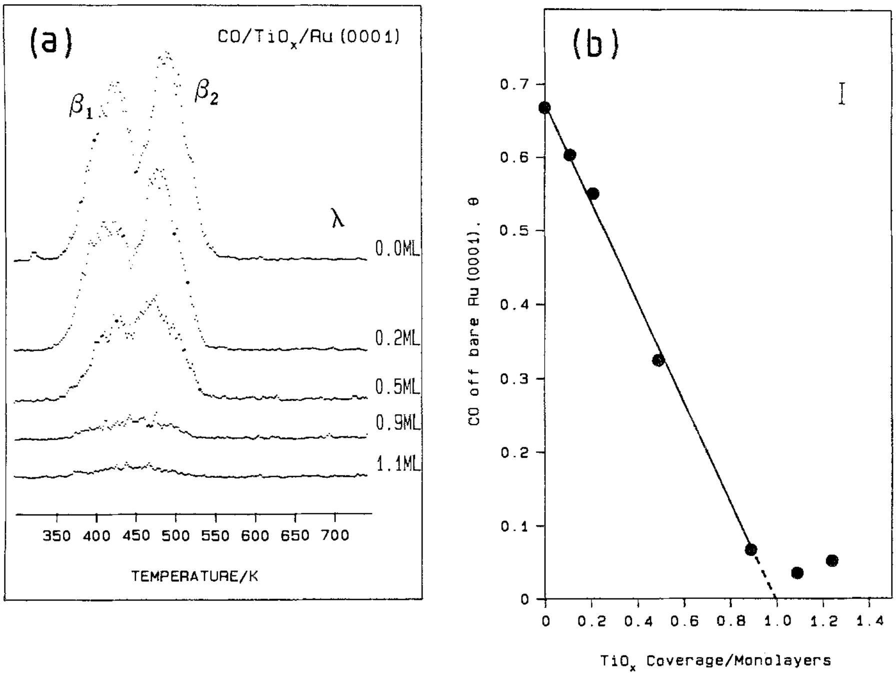

Fig. 4. (a) CO desorption spectra as a function of TiO$_x$ loading for non-annealed deposits. (b) TiO$_x$ dependence of integrated CO desorption yield derived from the data in (a).

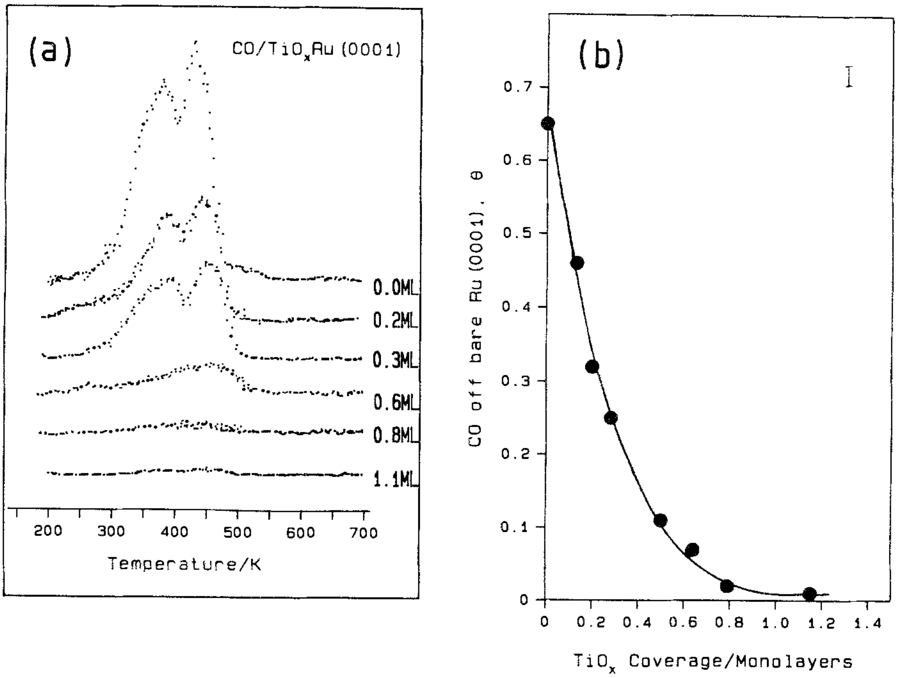

Fig. 5. (a) CO desorption spectra as a function of TiO$_x$ loading for deposits pre-annealed to 1100 K. (b) TiO$_x$ dependence of integrated CO desorption yield derived from the data in (a).

The corresponding results for CO uptake by Ru(0001) in the presence of $TiO_x$ deposits which had been pre-annealed to 1100 K are strikingly different from the above in three respects (fig. 5(a,b)). First, the complete suppression of $\beta$-CO chemisorption occurs at substantially reduced $TiO_x$ loadings; second, the inhibiting effect is markedly non-linear function of $TiO_x$ coverage (fig. 5(b)); third, there are pronounced *upward* shifts in both the $\beta_1$ and the $\beta_2$ peak temperatures in the presence of annealed $TiO_x$.

## 4. Discussion

Our results show that it is possible to set up the Ru(0001)/$TiO_x$ model system in ways which permit detailed examination of the various possible roles played by $TiO_x$ moieties on metal particles in the SMSI condition. We have also shown that the method and temperature of preparation of the $TiO_x$ film are critical in determining its subsequent structural and chemical properties. Such factors are likely to be of considerable significance in accounting for the discrepancies and disagreements which have arisen concerning the fundamental nature of the SMSI effect [23].

The observed layer-by-layer growth of $TiO_x$ on Ru(0001) at 300 K is consistent with efficient 'wetting' of the metal surface by the $TiO_x$ moieties. This state of the system does not involve any alloying between metal and $TiO_x$ and therefore provides a useful model for the decoration effect which has been put forward by some authors as an explanation for SMSI behaviour. In this condition, coverage by $TiO_x$ blocks CO chemisorption in a simple linear fashion; this is the type of response which is sometimes held to be responsible for SMSI behaviour [24,25].

However, when the initial $TiO_x$ loading exceeds a certain critical value and the system is heated to temperatures characteristic of the onset of SMSI, efficient diffusion of $TiO_x$ into bulk Ru occurs, *leaving behind an expanded monolayer film of a different type of $TiO_x$ phase*. The expansion of the overlayer which occurs on annealing $TiO_x$ loadings which are below the critical amount is consistent with mobility at the free surface being considerably greater than both bulk or grain boundary diffusion rates [14]. The LEED, Auger, XPS and CO chemisorption data are in good accord with the view that this new phase consists of a defective titanium monoxide which is formed on reduction of the initial $TiO_x$ layer by heating. The degree of reduction of defective titanium monoxides is proportional to the lattice parameter [17], a fact which is in excellent agreement with the LEED and Auger results. The presence of reduced Ti ions (XPS results) may be expected to lead to electronic charge transfer to neighbouring Ru atoms with a concomitant increase in CO binding energy at these sites – as is indeed observed. It also appears that this enhanced electronic interaction between the reduced $TiO_x$ film and the metal leads to more effective suppression of the *extent* of CO uptake, suggesting the operation of some kind of longer range effect. Such effects have indeed been invoked as an alternative explanation for the way in which metal sites are modified by $TiO_x$ in the SMSI state [26,27].

## 5. Conclusions

The structural, kinetic and chemical properties of $TiO_x$ films on Ru are critically dependent on initial loading and the temperature of preparation. At temperatures characteristic of the preparation conditions required for SMSI, excess $TiO_x$ diffuses into the bulk metal leaving an expanded, reduced titanium oxide film at the surface. Associated changes in CO chemisorption behaviour closely resemble those reported for supported catalysis in the SMSI condition.

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