PHYSICAL REVIEW B VOLUME 55, NUMBER 20 15 MAY 1997-II

Oxidation process in titanium thin films

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(Received 16 October 1996; revised manuscript received 7 January 1997)

The first stages of the oxidation process of titanium thin films deposited on top of Cu(100) substrates have been studied by means of Auger electron spectroscopy. Using principal component analysis we found different oxidation regimes for Ti films depending on their thickness. While for a film thickness up to 1 ML only one oxide phase (TiO_2) is present, in thicker films a new oxide phase (TiO_x; $x<2$) is detected. As the Ti film grows, the passivating effect of the titanium oxide stops the process of oxygen adsorption. Finally, for the thickest films (>7 ML) the effect of the interface turns out to be negligible and the oxidation characteristics of bulk titanium are recovered; i.e., only TiO_2 is detected again. [S0163-1829(97)05019-4]

I. INTRODUCTION

The study of titanium and its oxides, as well as the oxidation process, is a matter of current interest. Due to its intrinsic properties, titanium and titanium oxides are used in areas as different as catalysis, medicine, aircraft construction, corrosion, and so on. On the other hand, and in spite of the large amount of work devoted to the study of the surface oxidation process, there are several aspects of the process that are still not well understood.

The Ti oxidation kinetic is characterized by a fast oxygen adsorption followed by a slowing down of the process until saturation is reached. This experimental behavior has been explained in two different ways: (i) through a fast adsorption stage followed by a slow oxidation one[1] and (ii) through a fast oxidation stage followed by a slowing down due to the formation of a passivating film.[2,3] Another point of debate is the stoichiometry of the oxide film. The presence of several oxide phases has been reported in the literature, i.e., TiO,[4] TiO_2;[3,5–7] a mixture of TiO and TiO_2;[1] TiO_2 with minor quantities of other oxides also present;[2] TiO or Ti_2O_3;[8] TiO, Ti_2O_3, and TiO_2.[9] In a recent work,[7] based on the analysis of the Auger line shape, we found that the oxidation of titanium proceeds from the beginning of the process; i.e., no adsorption stage was detected and only titanium dioxide (TiO_2) is present along the whole process. On the other hand, a phase Ti_2O_3 was found when the process is undertaken at high temperatures ($T>500$ K).[10] In the present work, we study the oxidation process of titanium thin films. Here again the interest comes from applied and basic points of view. In the first case, thin-film titanium oxides are interesting as protective coatings against corrosion,[11] while, on the other hand, the transition from surfacelike to bulklike oxidation and the interface effect on the oxidation are subjects of current interest.

II. EXPERIMENTAL SETUP AND DATA TREATMENT

A. Experimental setup

The experiments have been carried out in an ultrahigh vacuum system with a base pressure in the 10^{-10}-Torr range, equipped with Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) facilities. The samples were prepared by Ti thermal evaporation on top of a high-purity copper monocrystal, oriented along the (100) axes. The copper surface was repeatedly cleaned by ion bombardment (Ar^+ 0.7 keV) and annealing at 850 K, until carbon and oxygen contamination was below the AES detection limit, and clear and narrow LEED spots were visible. Titanium was evaporated from a high-purity Ta-Ti alloy,[12] at a typical evaporation rate of 4×10^{-3} ML/s. The carbon and oxygen levels were kept below the AES detection limit along the whole film growth process. The AES spectra were acquired using a single-pass cylindrical mirror analyzer with a resolution of 0.6% and 2-V modulation amplitude. The primary beam energy was 3 keV, and to minimize electron-induced desorption effects the electron-beam density was kept very low (0.5 μA/mm^2). In this way, no electron-beam effect could be detected once the oxygen was evacuated from the UHV chamber. In addition, the electrons impinged the surface only during the acquisition of the Auger spectra. The oxidation of bulk Ti is pressure independent[7] at the low-pressures range. After checking this pressure independence for the thin-film regime we performed all the exposures at a constant pressure of 1×10^{-9} Torr, and raised it up to 1×10^{-8} Torr to obtain the saturation values (30 L; 1 $L=10^{-6}$ Torr s). The oxygen used was of high purity (better than 99.997%) and filled the whole UHV chamber. The pressure was measured by means of a noncorrected Bayard-Alpert gauge.

B. Data treatment

The method of principal component analysis[13] (PCA) has been successfully applied on different analysis techniques including AES.[14–21] The application of PCA in the sequential way to study chemical reactions occurring at surfaces, as well as to follow depth profiling of reactive interfaces, has been extensively discussed in our previous works.[7,10,19,20] Therefore, we will limit ourselves here to a brief description of the method.

In PCA one works with the covariance matrix (A) formed with the data matrix (D); $A=D^T\times D$. In any sequential process involving AES, such as in an oxidation study, D is an $m\times n$ matrix whose n columns are formed by the Auger

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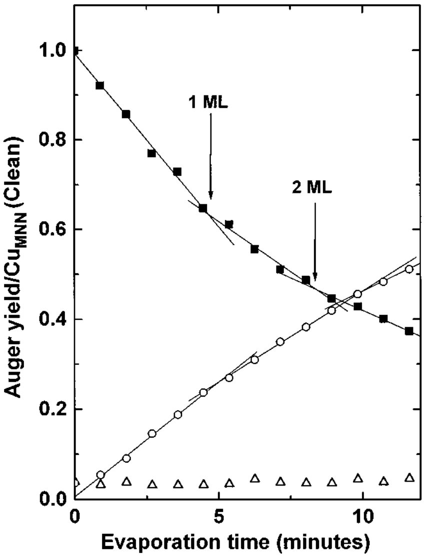

FIG. 1. Titanium, copper, and oxygen Auger yield (peak to peak) evolution [normalized to clean copper peak: Cu_{MNN}(60 eV)] vs titanium evaporation time. Cu_{MNN} (■); Ti_{LMM} (○); O_{KLL} (△).

spectra acquired sequentially during the experiment, with each spectrum being formed by m (energy) channels. The rank of A will be equal to the number of independent components of D. Therefore, for a set of perfectly noise-free spectra, the determination of the number c of independent chemical components is reduced to the determination of the number of nonzero eigenvalues of A. Since noise is always present in a real experimental case, all eigenvalues of A are different from zero. The key point in PCA is then the determination of those eigenvalues that have physical meaning, i.e., those eigenvalues that are statistically different from zero.[19]

The last step in this method is the decomposition of the data matrix into a product of two matrices, in such a way that one matrix contains the Auger spectra of the pure components and the other one their relative weights.[13,15,19] This step, the so-called target transformation method (TT), requires additional information. In the conventional TT one needs to know the concentration of $c-1$ components in at least one point of the profile. On the other hand, in the sequential method, the number of eigenvalues is fixed and the evolution of the error performed in reproducing the data matrix is followed as a new spectrum is added to the experimental sequence.[19] Each time the error in reproducing the data matrix with N fixed independent factors turns out to be larger than the experimental error, it is necessary to assume the existence of a new factor in the process; i.e., from this point the system must be characterized by the presence of $N+1$ components.

III. RESULTS

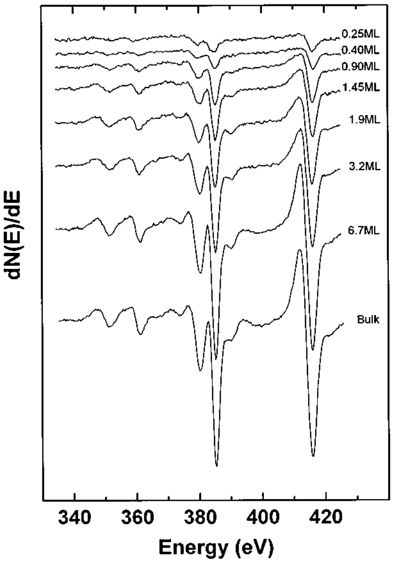

FIG. 2. Ti Auger line shape evolution for a set of films of different thickness over Cu(100).

In Fig. 1 we show the peak-to-peak intensities corresponding to the Ti_{LMV} (418 eV) and Cu_{MNN} (60 eV) Auger transitions as a function of the Ti evaporation time. The intensity of the O_{KLL} transition is also plotted to show the low level of contamination achieved along the whole film growing process. The breaks observed in the time evolution of both Cu and Ti peaks correspond to the completion of successive layers.[22] The lines are least-square fits to the experimental data. This result shows a layer-by-layer growth of Ti over Cu(100), in agreement with the findings of Vähäcangas, Williams, and Park[23] over Cu(111). The curve shown in Fig. 1 is used in this work as a calibration curve to determine Ti film thickness. A Ti evaporation rate of around 4×10^{-3} ML/s is obtained from the figure for the calibration conditions.

In Fig. 2 we show the evolution of the Ti Auger line shape as a function of the film thickness. The Ti_{LMV} transition line shape dependence on film thickness is apparent from these results. Since this transition involves electrons from the valence band, one can conclude that this Ti_{LMV} dependence is related to a charge transfer between Ti and Cu and that this charge transfer is film thickness dependent. Results in close agreement with these findings have been presented for the system Ti/W by Herman and Peden.[24]

In Fig. 3 we show, through the O_{KLL} Auger peak, the evolution of the oxygen amount at the surface as a function of the oxygen exposure, for a set of different Ti film thicknesses. In this figure, the results for pure bulk titanium and copper surfaces are also included. Comparing the results for pure Cu and Ti, one can observe the large difference in the chemical activity for both of these metals in the presence of oxygen. The oxygen evolution in the Ti thin film regime shows a behavior similar to the bulk oxidation process, i.e., an initial fast increase of the oxygen content at the surface followed by a slowing down and a plateau. These stages are clearly dependent on the Ti film thickness.

In Fig. 4 the oxygen saturation value as a function of the Ti film thickness is displayed. The amount of oxygen at the surface has been corrected for coverages below 1 ML to consider only the oxygen adsorption at the titanium surface. To do that we use the results shown for pure copper in Fig. 3, and assume that the oxygen adsorption process on copper is independent of the presence of titanium. The straight lines drawn in this figure correspond to the theoretical O_{KLL} Auger

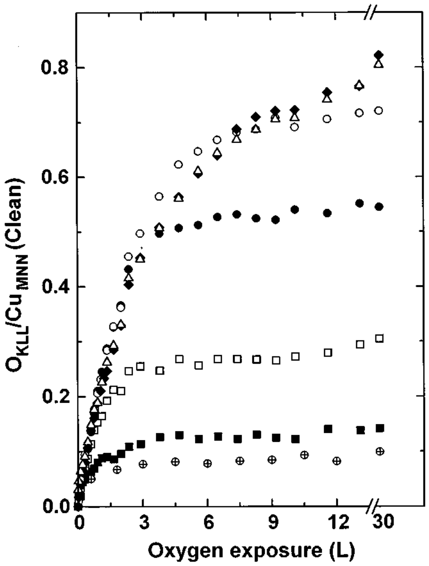

FIG. 3. Oxygen evolution (O_{KLL} peak to peak) vs oxygen exposure for different Ti film thicknesses. In ML, 0 (Cu clean) (⊕); 0.25 (■); 0.75 (□); 1.45 (●); 3.2 (○); 6.7 (◆); Ti bulk (△).

signal expected on the basis of layer-by-layer growth of stoichiometric titanium dioxide. The outcoming Auger electrons are only affected by the attenuation due to the finite escape depth, i.e., $\exp(-\alpha)$ where α is the attenuation coefficient [$\alpha = d/\lambda \cos(\theta)$, d is the film thickness, θ the emission angle, and λ the Auger escape depth]. Within this model one expects a linear dependence of the O_{KLL} Auger yield with film thickness, separated by breaks corresponding to the completion of each monolayer, just like the behavior observed for Ti in Fig. 1. A value of $\alpha = 0.42$ for the oxygen Auger electrons through titanium oxide is obtained based on measurements of the attenuation of the copper Auger signal through the same oxide film, and assuming an energy dependence $E^{1/2}$ for the Auger escape depth.[25] The behavior of the oxygen saturation value with film thickness starts to deviate from this model after a coverage of about 2 ML. This result points either to the passivating nature of the Ti oxide film, or to the presence of oxide phases with lower stoichiometries.

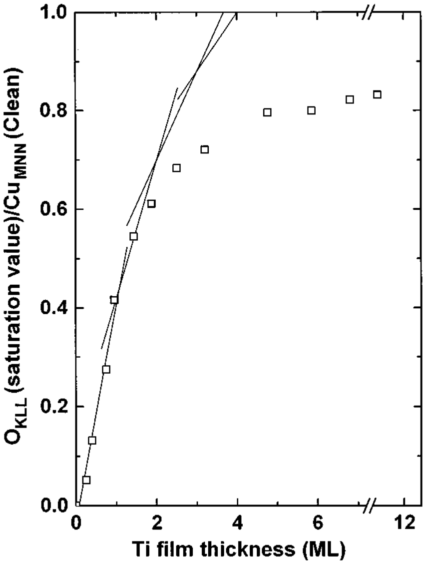

FIG. 4. Saturation value of the oxygen amount at the surface as a function of the titanium film thickness (□). Straight lines represent TiO_2 growing layer by layer.

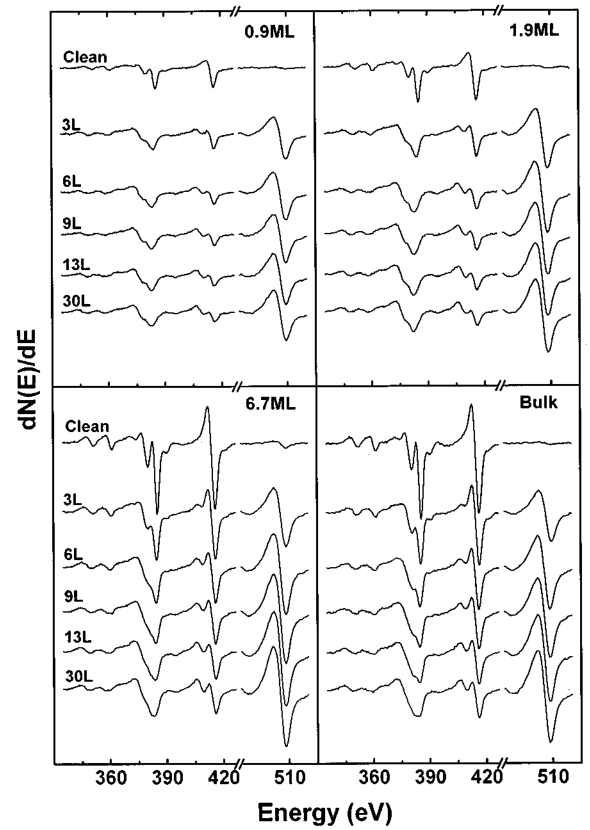

FIG. 5. Ti_{LMM}, Ti_{LMV}, and O_{KLL} Auger line shape evolution for a set of films of different thicknesses over Cu(100), as function of the oxygen exposure.

In Fig. 5 we show the evolution of the Ti and oxygen Auger line shapes for four different Ti films, ranging from below 1 ML to bulk, as a function of the oxygen exposure. In these figures the capability of AES to detect chemical changes and the Ti_{LMV} dependence on film thickness are evident. One startling point is the evolution of the Ti Auger line shape for 0.9 and 1.9 ML. In fact, although the starting point is clearly different, showing the dependence of the charge transfer between Ti and Cu on film thickness, already discussed, the final shapes are quite similar to the line shape of TiO_2. This result suggests that the interaction Ti-O is so strong that the Ti-Cu charge transfer becomes irrelevant.

Based in the fact that only one of the main Ti Auger transitions involves valence electrons (Ti_{LMV}), it has been proposed that the ratio between Ti_{LMV} and Ti_{LMM} Auger yield, hereafter called Ti_{VM}, can be used as a good indicator of the Ti oxidation state.[4,26] However, we have already shown[7] that the analysis of this ratio, without taking into account the variations of the Auger line shape, can lead to erroneous conclusions. In the particular case of Ti oxidation, while the analysis of the Ti_{VM} evolution ratio suggests the presence of an adsorption stage[4] (no chemical reaction) in the process, a careful study of the Auger line shape through factor analysis shows that the oxidation of Ti proceeds from the very beginning of the process.[7] In spite of this, it is clear

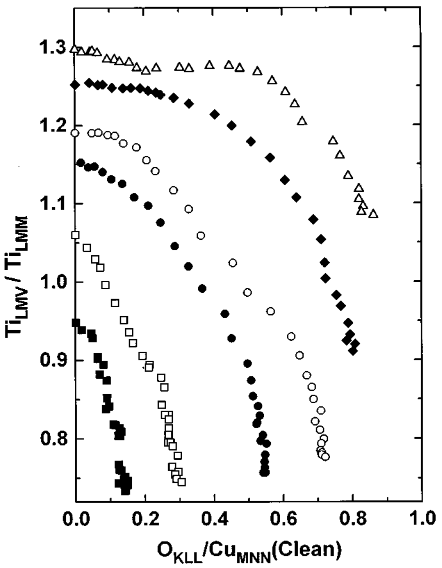

FIG. 6. $\mathrm{Ti}_{LMV}/\mathrm{Ti}_{LMM}$ ratio as a function of the oxygen amount at the titanium surface for different Ti film thicknesses: In ML, 0.25 (■); 0.75 (□); 1.45 (●); 3.2 (○); 6.7 (◆); bulk (△).

that the evolution of the Ti_{VM} ratio can be used as a first indicator for a qualitative analysis. In Fig. 6, we show the evolution of the ratio Ti_{VM} versus the amount of oxygen at the surface. It is clear that, within the Ti_{VM} picture, the oxidation process is strongly dependent on film thickness. The first startling result in Fig. 6 is the film thickness dependence of the stationary stage of Ti_{VM}, i.e., the stage where no variation of Ti_{VM} with oxygen exposure is observed. This stationary stage, as mentioned above, has been associated with the oxygen adsorption stage.[4] As can be observed in Fig. 6, this adsorption stage tends to disappear for the thinnest films. Since we have already shown that titanium dioxide is formed from the very beginning of the process,[7] this indicates that the ratio between adsorbed and reacted oxygen, i.e., the initial Ti reactivity, depends on film thickness.

Another interesting result shown in Fig. 6 is the already pointed out film thickness dependence of the Ti_{LMV} Auger transition for pure Ti films. This dependence on Ti film thickness appears in this figure as having a different starting value for the Ti_{VM} ratio (no oxygen at the surface). On the other hand, the saturation value of Ti_{VM} is also dependent on film thickness. This fact may be due to different sources: (i) the different Ti_{VM} starting value, (ii) a ratio among different oxide phases depending on the film thickness, and (iii) a different ratio among TiO_2 yield coming from the oxide film and Ti Auger yield coming from the subsurface, i.e., different oxide thickness. Thus, the analysis of the evolution of the Ti Auger line shape (Fig. 5) and the ratio between both Auger transition lines of Ti (Fig. 6) suggests the presence of interesting effects, although they seem unable to provide quantitative answers. In order to obtain such an answer we are required to analyze quantitatively the evolution of the complete Auger line shape, and for that purpose the principal factor analysis is a good tool.

The oxidation kinetics of titanium, going from below 1 ML to bulk, shown in Figs. 2–6, may be summarized as follows: (i) Two oxidation regimes occur: fast oxygen incorporation followed by a slowing down until saturation. (ii) The oxygen saturation content depends on Ti film thickness. The linear dependence of the O_{KLL} Auger yield versus Ti coverage shows a layer-by-layer growth of this titanium oxide phase up to 2 ML, followed by a slowing down. (iii) There is a lack of an adsorption stage for the thinnest films in the Ti_{VM} picture, as well as different final oxidation states within the same picture.

IV. DISCUSSION

As the main interest of the present work is the study of the oxidation process of Ti thin films, it is crucial to work with a substrate that acts as an effective barrier for the oxygen migration and allows the growth of films with minimum distortions. From the point of view of an oxygen migration barrier, an oxide substrate (TiO_2, for instance) would be ideal. However, in this case the interaction of the growing Ti film with the substrate oxygen could not be neglected.[24] The use of a Cu substrate minimizes, but does not eliminate completely, the metal-metal interaction, as can be observed in Fig. 2. In any case this represents a good enough barrier for oxygen migration, as observed from the results in Fig. 3. On the other hand, Ti by itself acts as a barrier for oxygen migration (passivating coating film) as shown for bulk Ti (Ref. 7) and Ni.[27] Based on these facts, we analyze our results on the basis of a pure interaction between oxygen and titanium considering copper as an inert substrate as long as the Ti oxidation process is concerned. Supporting our model, the linear ratio between the oxygen amount at the surface and the titanium coverage below 1 ML (Fig. 4), suggests the existence of a local effect; i.e., the enhancement of oxygen incorporation occurs at the titanium growing film.

There are two different effects involved in the saturation of the oxygen incorporation observed in Figs. 3 and 4. In fact, while the saturation of the oxygen at the surface for the thinner films is due to the exhaustion of metallic titanium, i.e., the oxidation process stops when all the titanium has reacted, the saturation for the thicker films occurs when a passivating oxide film has been developed at the titanium surface. Although the same oxygen evolution at the surface for thicker films could be explained through the penetration of oxygen beyond the Auger electron escape depth, we have already shown[7] that the developing of the passivating film is responsible of the saturation stage for the bulk case. This demonstration was based in the detection of metallic titanium after saturation has been reached.

By studying the oxidation process for bulk titanium we found only one oxide phase (TiO_2) at room temperature,[7] and the appearance of $\mathrm{Ti}_2\mathrm{O}_3$ when the oxidation was performed at high temperatures.[10] In Fig. 4 we observe a linear relationship between the saturation oxygen and the film thickness for films below 2 ML. This suggests the layer-by-layer growth of a unique oxide phase at saturation for these coverages. On the other hand, for thicker films a slowing down of the (oxygen/titanium) slope is observed, suggesting a change in the oxidation kinetics. To gain information about the oxidation process involving thin films we analyze the information contained in the Auger line shape. To do that we apply the principal component analysis and target transformation methods.

The study of the oxidation kinetic represents an ideal case

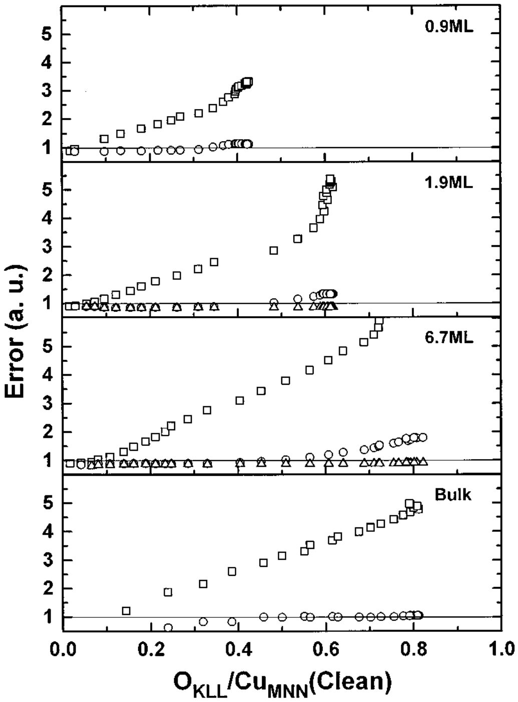

FIG. 7. Error evolution within the PCA sequential analysis vs oxygen amount at the surface, for a set of different film thicknesses: considering only the first factor (□); adding a second factor (○), and including the third factor (△).

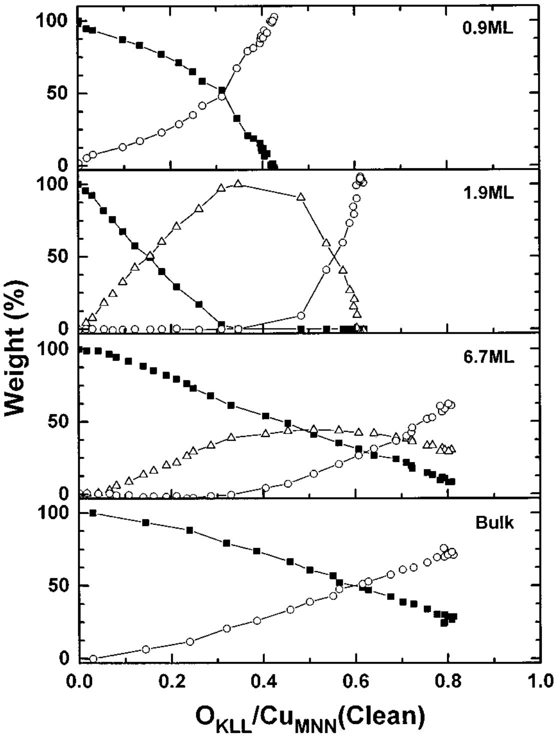

FIG. 8. Evolution of the weights of the different factors after target transformation analysis for the same set of thicknesses as shown in Fig. 7, vs oxygen uptake at the surface. Ti (■); TiO_2 (○) and TiO_x (△).

for applying the PCA method in the sequential way. In Fig. 7 we show the evolution of the error obtained in reproducing the data matrix using one, two, and three factors for the oxidation process of a set of different Ti films. This error is shown as a function of the oxygen coverage and it is compared to the experimental error. Following the sequential PCA analysis, as detailed in Sec. II, each time the calculated error turns out to be larger than the experimental one, a new oxide phase enters in the oxidation process. From the results shown in Fig. 7, it appears that the entire oxidation process can be accounted for by using only three different factors. Since the first one corresponds to metallic titanium, only two different oxide phases appear along the whole process. Moreover, for the thinner films, as well as for the bulk, only one oxide phase is detected.

In Figs. 8 and 9 we show the results corresponding to the TT analysis for the oxidation of Ti films for a set of different film thicknesses. In Fig. 8, the weight of each Auger line in the total Auger line shape versus the oxygen amount at the surface is depicted, and in Fig. 9 we show the Auger line shapes obtained from TT analysis, corresponding to the three factors appearing along the oxidation process. In this figure, the experimentally obtained Auger spectra for titanium and its most common oxides[28–31] are also shown. Using these spectra as fingerprints we can identify the different factors appearing in the oxidation process of Ti. Based on the PCA analysis we conclude that the oxidation of thin Ti films is a complex process where more than two stages can be identified. For films below 1 ML only one oxide phase is formed (TiO_2). For films between 1 and 2 ML, a lower oxide state is formed during the process ($TiO_{x<2}$), but at saturation only TiO_2 remains. For thicker films this lower oxidized phase remains after saturation. Finally, for bulk conditions the same behavior as for the thinnest films is recovered; i.e., only TiO_2 is formed.

Although the experimental conditions are quite different (they grow Ti oxide films by evaporating Ti in an oxygen atmosphere) one is tempted to compare our results with those of Boffa *et al.*[32] Within their scheme, the Ti-Cu bonds are responsible, through the lowering of the oxidizing ability of titanium, for the existence of the lower oxide phase of Ti ($TiO_{x<2}$). Additional support for this mechanism is given by the already mentioned experimental fact that the valence band of Ti is affected by the presence of Cu. For thicker films the Ti-Cu bonds (the interface) are far from the surface and consequently they turn out to be less relevant to the oxidation process. Finally, for the thickest films the bulk oxidation conditions are recovered.

The effect of the interface on the oxidation process, as it is pictured by the analysis of PCA, seems to be a bit more complex. In fact we found that the oxide phase at coverages below 1 ML corresponds just to titanium dioxide. On the other hand, although the lower oxidized phase ($TiO_{x<2}$) is detected during the oxidation process for films between 1 and 2 ML, it remains at saturation only for films thicknesses beyond 2 ML.

The PCA results suggest an oxidation kinetics as follows: (i) Although the bond Ti-Cu retards the formation of the Ti valence band, the O-Ti bond is so strong that for film thicknesses below 1 ML the most oxidized phase of titanium is formed. (ii) The formation of the lower oxidized phase of Ti ($TiO_{x<2}$) is a consequence of two coexisting phenomena; the depletion of electrons of the Ti valence band due to the

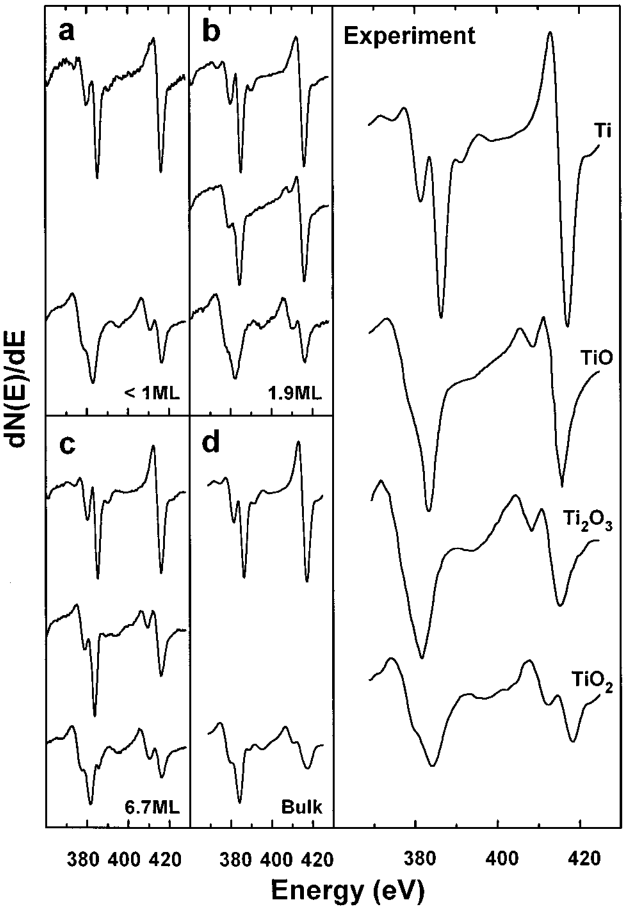

FIG. 9. (a)–(d) Auger line shape obtained from target transformation analysis for the same set of Ti films as in Figs. 7 and 8. Experimental: experimental Auger line shape for Ti (Ref. 28), and its different oxides; TiO (Ref. 29), Ti_2O_3 (Ref. 30), and TiO_2 (Ref. 31).

interaction with the substrate and the passivating effect of the formed surface oxide. Both effects tend to lower the oxygen migration ability, allowing the survival of the lower oxidized state of titanium. It is clear that this combined effect is operative only for intermediate film thickness. For the thinner films no passivating effects are expected and for the thicker ones no electron depletion of the valence bands exists in the surface region. Finally, the $TiO_{x<2}$ layer is located immediately below the oxide film, i.e., between the TiO_2 film and the Cu substrate for the thinner films, but between the TiO_2 film and Ti for the thicker ones. This fact is clearly seen in Fig. 6 where these three factors coexist, i.e., Ti, $TiO_{x<2}$, and TiO_2. Since we always observe the metallic film below the oxide one, it is clear that any explanation based on the (finite) escape depth of Auger electrons compared to the oxygen penetration depth should be disregarded. Although this result is clearly different from that of Boffa *et al.*,[32] who detected $TiO_{x<2}$ only at the interface, there are no serious discrepancies between both these results since in their experimental setup no oxygen migration is involved.

Finally, the extension of the substrate influence to beyond 6 ML is in agreement with the results of Vähäcangas, Williams, and Park,[23] who found that for Ti films on Cu(111) the LEED pattern of Ti is observed only for films thicker than 6 ML.

V. CONCLUSION

AES and PCA have been used to study the oxidation mechanisms for Ti thin films and compared to the Ti bulk process. We found that for low coverages (<2 ML) only TiO_2 is detected after the oxygen saturation. For thicker films we detected a lower oxidized phase of Ti ($TiO_{x<2}$), which finally disappears for Ti bulk conditions. We associate the formation of the $TiO_{x<2}$ phase to the depletion of the Ti valence band due to the interaction Ti-Cu combined with the passivating effect of the TiO_2 film. We found that the film thickness needed to achieve bulk conditions for the oxidation process, as well as to recover the Auger characteristic ratio between Ti Auger transitions, occur well over 6 ML.

ACKNOWLEDGMENTS

This work has been financially supported through PID 3748 from CONICET and CAI+D E02 and E12 from UNL. We wish to thank Dr. R. Vidal for useful discussions and Professor M. C. G. Passeggi for his suggestions.

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