Electronic structure of stoichiometric and reduced Ta$_2$O$_5$ surfaces determined by resonant photoemission

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The electronic properties of stoichiometric and reduced Ta$_2$O$_5$ thin films have been studied with resonant photoemission using synchrotron radiation. It was found that Ar$^+$ bombardment induces electronic states in the band gap region and an attenuation of the overall valence band. These changes are associated with the formation of oxygen vacancies during the reduction of the surface by Ar$^+$ bombardment. For both stoichiometric and Ar$^+$-bombarded Ta$_2$O$_5$ films, resonant photoemission from the valence band was observed when the photon energy was in the neighborhood of the Ta $5p \rightarrow 5d$, $5p \rightarrow 6sp$, and $4f \rightarrow 5d$ transition energies. The constant initial-state curves show multiple resonance maxima that are explained in terms of the Ta $5p \rightarrow 5d$, $5p \rightarrow 6sp$, and $4f \rightarrow 5d$ photoabsorption mechanisms, the spin-orbit splitting of the Ta $5p$ and Ta $4f$ core levels, and the splitting of the Ta $5d$ final states by crystal-field interactions. Contrarily to $3d$ and $4d$ transition metals no differences have been found in the resonance behavior of the valence-band features lying in the ~ 4–10-eV range. This is attributed to the more extended nature of Ta $5d$ and $6sp$ orbitals with respect to $3d$ and $4d$ cationic orbitals.

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I. INTRODUCTION

Tantalum oxide has received much attention due to its chemical stability and technological applications. In particular, Ta$_2$O$_5$ films have been used as high-temperature materials, antireflection coatings for solar cells, high dielectric constant insulators in microelectronics, etc. In microelectronic applications, special attention has been addressed to the presence of oxygen vacancies in thin Ta$_2$O$_5$ insulator films, since oxygen vacancies are considered to be one of the main reasons of the leakage current.[1] Therefore the study of the electronic structure of stoichiometric and nonstoichiometric Ta$_2$O$_5$ films is of great importance from both the technological and fundamental points of view. Ta$_2$O$_5$ has a complex structure containing the octahedra, TaO$_6$, and the pentagonal bipyramids, TaO$_7$, both being strongly distorted.[1] The electronic structure of tantalum oxide has been investigated by x-ray photoelectron spectroscopy (XPS),[2,3] ultraviolet photoelectron spectroscopy (UPS),[4] Auger electron spectroscopy (AES),[5,6] electron energy-loss spectroscopy (EELS),[5,6] bremsstrahlung isochromat spectroscopy (BIS),[7] and x-ray-absorption spectroscopy (XAS).[8] In addition, several band-structure calculations have been published for stoichiometric and nonstoichiometric (with oxygen vacancies) Ta$_2$O$_5$.[1,9] However, resonant photoemission experiments, which can provide useful information about its electronic structure, have not been performed.

Resonant photoemission in $3d$ transition metals (TM's) has been the subject of many recent experimental and theoretical investigations.[10] The phenomenon is usually explained as due to an interference effect between the direct photoemission process and autoionization of a highly localized excited state created by photoabsorption. It is observed when the energy of incident photons is varied around the threshold for a $p \rightarrow d$ transition. The resonance has been also found in $3d$ and $4d$ TM compounds (nitrides and oxides) where the d band is completely suppressed. In such cases, it is explained as due to the hybridization between the O $2p$ or N $2p$ and cation d orbitals, and therefore resonant photoemission is used to isolate the d-states contribution and to study the valence band (VB) structure of TM compounds.[11–21] However, the number of works dealing with resonant photoemission on $5d$ TM and TM compounds is rather scarce.[22–27] In particular, only the oxygen deficient WO$_3$ oxide has been studied by resonant photoemission.[26] Therefore the aim of this work is to study the VB electronic structure of stoichiometric and reduced Ta$_2$O$_5$ surfaces by resonant photoemission to determine its cationic character.

II. EXPERIMENT

The experiments were performed at LURE (Orsay, France) using the PES2 experimental station connected to the SU8 ondulator beamline of the Super-Aco storage ring. The measurements were carried out in an ultrahigh vacuum system, with a base pressure better than 1×10^{-10} Torr, equipped with an angle resolving 50-mm hemispherical VSW analyzer coupled to a goniometer inside the chamber. For a photon energy ($h\nu$) in the range 20–70 eV, the overall energy resolution, including the analyzer, was estimated to be better than 0.1 eV. Photoemission spectra have been normalized to the incident current measured in a gold grid located at the entrance of the chamber.

A 5N oxygen exposure of 36 000 L (1 L$=10^{-6}$ Torr s) at 823 K was applied to a 99.99% purity tantalum foil to obtain the stoichiometric Ta$_2$O$_5$ surface. The reduced oxide was prepared by Ar$^+$ bombardment of the stoichiometric Ta$_2$O$_5$ during 10 min at 0.5 keV.[28]

III. RESULTS

Figure 1 shows the valence-band spectra, after background subtraction, of (a) stoichiometric and (b) reduced
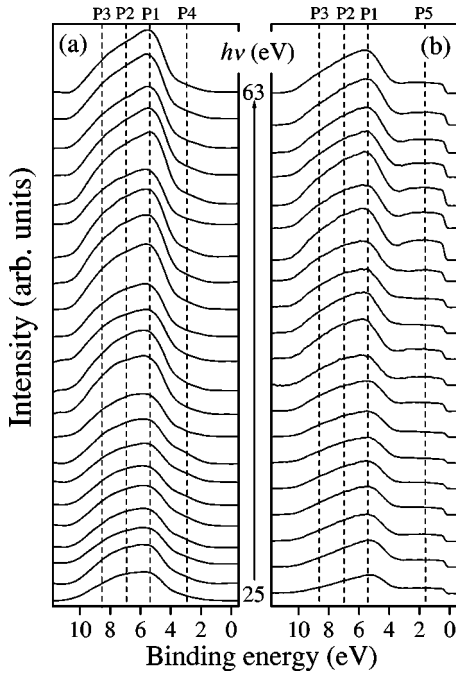
FIG. 1. Valence-band spectra of (a) stoichiometric and (b) Ar$^+$-bombarded Ta$_2$O$_5$ as a function of the binding energy for photon energies in the range $h\nu = 25$–63 eV. Spectra are shown every 2 eV. The different features are indicated by dotted lines.

FIG. 2. Intensity of the difference spectra calculated by subtraction of the spectra measured at $h\nu = 25$ eV (off resonance) from all measured spectra, as a function of binding energy and photon energy, for (a) stoichiometric and (b) reduced Ta$_2$O$_5$.

FIG. 3. CIS curves obtained from Fig. 2 corresponding to P1, P2, P3, P4, and P5 features of the valence band, for (a) stoichiometric and (b) reduced Ta$_2$O$_5$. The $4f_{7/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ core thresholds, and the unoccupied $5d(t_{2g})$, $5d(e_g)$, and $6sp$ states above E_F in Ta$_2$O$_5$ have been indicated by arrows.

Ta$_2$O$_5$ surfaces measured at different photon energies between 25 and 63 eV. For simplicity spectra are displayed every 2 eV. The VB of stoichiometric Ta$_2$O$_5$ is characterized by a broad band formed by the hybridization of O $2p$, Ta $5d$, and $6sp$ atomic orbitals.[9] This band peaks at ~ 5.5 eV, with a shoulder in the high binding-energy (BE) side. The VB intensity falls to zero at the Fermi level E_F and only some weak emission can be observed in the band gap at ~ 3 eV, which is probably associated with trapped electrons in oxygen vacancies and surface defects caused by the preparation method used.[16] In addition to that, occupied states appear in the band gap up to E_F, and an overall attenuation of the VB is observed, as a consequence of oxygen loss during reduction of the stoichiometric Ta$_2$O$_5$ surface by Ar$^+$ bombardment [Fig. 1(b)].

As shown in Fig. 1, the total intensity and the relative intensities of the different VB features depend on the photon energy due to resonance processes. To emphasize the resonance behavior of the VB, difference spectra between all measured spectra and the spectra corresponding to $h\nu = 25$ eV (off resonance) have been calculated. The results are plotted in Fig. 2 as a function of the binding energy and $h\nu$. In this figure, the intensity is maximum for the darkest feature and minimum for the brightest. In order to study separately the resonant photoemission of the different VB features, constant-initial-state (CIS) curves at binding energies of 5.4 eV (P1), 7 eV (P2), 8.6 eV (P3), 3 eV (P4), and 1.6 eV (P5) have been obtained from Fig. 2, and plotted in Fig. 3 as a function of $h\nu$. Although the resonance behavior shown in Fig. 3 is rather complex, similar evolutions are found for all the VB features in both stoichiometric and re-
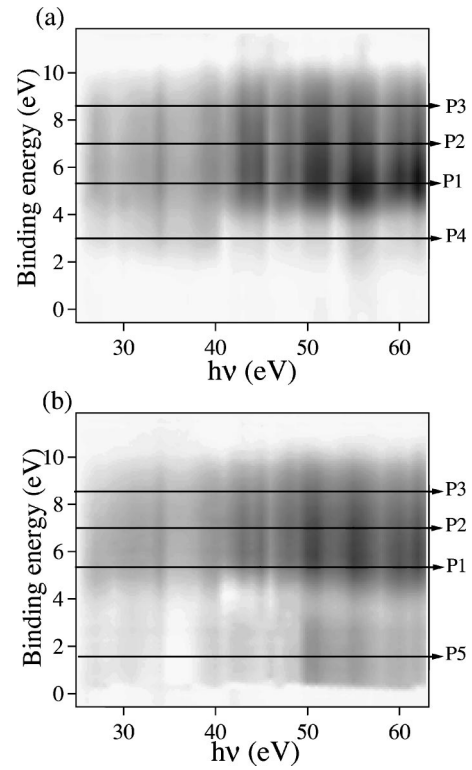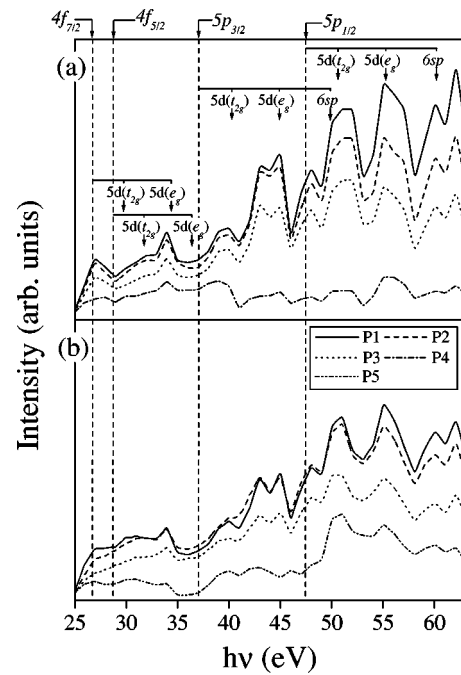
duced Ta_2O_5 surfaces. The $4f_{7/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ core thresholds in Ta_2O_5 have been indicated in Fig. 3.[3,5] In addition, the unoccupied $5d(t_{2g})$, $5d(e_g)$, and $6sp$ states above E_F, as determined by BIS and O 1s XAS, are also indicated.[7,8]

IV. DISCUSSION

The overall shape of the VB of stoichiometric Ta_2O_5 in Fig. 1 is well explained using the calculated density of states (DOS) of Khanin and Ivanovskii using the X_αSW method.[9] According to these authors, the VB is formed by the hybridization of O 2p and Ta 5d-6sp states, and the bond populations between O 2p and Ta 5d, 6p, and 6s atomic orbitals are 6.21, 2.37, and 0.21, respectively. Bond populations show that the O 2p and Ta 5d atomic orbitals are the most hybridized, but a non-negligible contribution from hybridization between O 2p and Ta 6sp is also found.

Reduction of the Ta_2O_5 surface by Ar^+ bombardment causes a decrease of the overall intensity of the VB in the ~ 4–10-eV region, that is more pronounced in the high BE region. In 3d and 4d TM oxides, this high BE region has been usually attributed to O 2p-TM d bonding states.[15,16] In addition, the band gap region becomes populated up to E_F. These changes are associated with the formation of oxygen vacancies by Ar^+ bombardment, which causes a decrease of the hybridized O 2p-Ta 5d, 6sp occupied states in the 4–10-eV region, and an increase in the band-gap population of Ta 5d derived states. Theoretical calculations of Sawada and Kawakami have predicted the formation of occupied states just below E_F by the presence of oxygen vacancies in Ta_2O_5.[1] The formation of cationic-derived occupied states in the band gap related to oxygen vacancies was also found during Ar^+ bombardment of other stoichiometric TM oxides.[15,16,26]

Resonant photoemission in tantalum and tantalum oxide has been recently predicted.[5] It was also studied, on polycrystalline Ta, by Raaen in the photon energy range of 35–62 eV.[23] Raaen found that the Ta 5d emission is resonantly enhanced above the $5p_{3/2}$ and $5p_{1/2}$ core thresholds, for photon energies of $\sim$ 40 and 50 eV, respectively. CIS curves showing two maxima have been also found in TaC by Anazawa *et al.*[25] and in $TaSe_2$ by Sakamoto *et al.*[22] They are explained taking into account the $\sim$ 10-eV spin-orbit splitting of the Ta 5p band. However, the CIS curves found in this work for stoichiometric and reduced Ta_2O_5 are rather complex showing several maxima, even at photon energies below 40 eV. It is important to observe that resonant photoemission in TM's and TM compounds has been observed when the energy of incident photons is varied around the threshold of a $p \rightarrow d$ transition.[11–26] However, resonant photoemission at the $4f \rightarrow 5d$ transition threshold has been proposed to explain the autoionization emission features observed in electron bombarded tantalum and tantalum oxide.[5] Furthermore, it was also observed in photoemission studies of Pt near the 4f threshold.[27]

In order to explain the shape of CIS curves in Fig. 3, photoabsorption processes for the Ta $5p \rightarrow 5d$, $5p \rightarrow 6sp$, and $4f \rightarrow 5d$ transitions will be considered. It should be noted that, according to dipole selection rules, the Ta 6p derived states are not involved in the $5p \rightarrow 6sp$ transition. Also, the $4f \rightarrow 6sp$ transition is dipole forbidden. The spin-orbit splittings for the Ta 4f and 5p bands in Ta_2O_5 are $\sim$1.8 and 10.4 eV, respectively.[3,5] In addition, the structure of the unoccupied Ta 5d and 6sp states above E_F should be also taken into account. Due to the crystal-field interaction, the splitting of the Ta 5d unoccupied bands, t_{2g} and e_g, is 4.6 eV. The unoccupied Ta 6sp states are 9.5 eV above the lower t_{2g} state[7,8] (see schematic diagram in Fig. 3). Therefore the combination of the spin-orbit splitting of the Ta 5p and 4f core levels, and the splitting of the final d states by crystal-field interactions allows us to explain satisfactorily the experimental CIS curves, as can be observed in Fig. 3.

The spin-orbit splitting of the core level has been observed in the CIS curves of Ta, TaC, $TaSe_2$, CuHf, and oxygen deficient WO_3 surfaces for the $5p \rightarrow 5d$ transition.[22–26] On the other hand, both the core-level spin-orbit splitting and the crystal-field splitting of the final d states have been also resolved in the CIS curves of TiO_2 for the Ti $2p \rightarrow 3d$ transition by Prince *et al.*[20] As pointed out by these authors, resonant photoemission allows us to obtain qualitatively the XAS spectrum projected on a particular VB feature. For Ti and TiO_2, the resonance effects display a broader structure for the $3p \rightarrow 3d$ transition than for the $2p \rightarrow 3d$ transition.[20,29] Kaurila *et al.*[29] have attributed the broadening of the resonant region in Ti at the $3p \rightarrow 3d$ transition to shake-up excitations occurring coincidentally with the core excitation. Shake-up processes would be much smaller for the $2p \rightarrow 3d$ resonance as a consequence of the large energy difference between the $2p \rightarrow 3d$ transition and the shake-up excitations from the VB to an unoccupied band. Therefore the narrowness of the observed resonances in stoichiometric and reduced Ta_2O_5 surfaces suggests a low cross section for shake-up excitations for the Ta $5p \rightarrow 5d$ and Ta $5p \rightarrow 6sp$ transitions. For the Ta $4f \rightarrow 5d$ transition, the four expected maxima in the CIS curves are not fully resolved. This is due to the small Ta 4f spin-orbit splitting, and to the small Ta 4f photoionization cross section with respect to that of Ta 5p core levels.[30] For Pt, the larger 4f spin-orbit splitting ($\sim$3.6 eV) has been resolved in the CIS curves by Williams *et al.*[27]

A $np \rightarrow (n+1)s$ transition has been also proposed to explain maxima at higher photon energies in the CIS curves of TiO_2, ZrO_2, and MoS_2.[15,16,31] However, it should be noted that the O 2p-Ta 6s bond population is not high enough to explain the observed enhancement for the Ta $5p_{1/2} \rightarrow$ Ta 6sp transition, above all for the stoichiometric surface. The proposed Ta $5p_{1/2} \rightarrow$ Ta6sp resonance enhancement, isolated from other contributions, can be observed in Fig. 3 for all the VB features, even for the P5 band-gap feature of the reduced surface. As observed in Fig. 3, the absolute resonant enhancement of the P1-P3 VB features decreases with Ar^+ bombardment as a consequence of the increase in the population of the unoccupied Ta 5d states in the band gap due to the oxygen loss during reduction of the surface. In addition, the P1-P3 relative enhancements for the Ta $5p_{1/2} \rightarrow$ Ta 6sp transition with respect to the enhancements for the other

transitions decrease with Ar^+ bombardment. This fact seems to be also related to the oxygen loss suggesting that an inter-atomic direct recombination,[13,17] in which the anion $2p$ states would resonate themselves, should be a complementary mechanism for the proposed Ta $5p_{1/2} \rightarrow$ Ta $6sp$ enhancement. However, this explanation is very controversial and the exact mechanism remains unknown. Moreover, it should be noted that this resonance is also observed for the induced band-gap states of predominant Ta $5d$ character. It should be pointed out that the Ta $5p_{3/2} \rightarrow 5d$, $5p_{1/2} \rightarrow 5d$, $4f_{7/2} \rightarrow 5d$, and $4f_{5/2} \rightarrow 5d$ core excitations have been also observed in the EELS spectra of Ta_2O_5 and 30 L oxygen exposed Ta, but the splitting of the $5d$ unoccupied final states has not been resolved.[5,6] Likewise, the autoionization features associated with these core excitations have been also found in the low-energy AES spectra.[5,6] However, no features in the EELS spectra associated with the Ta $5p_{1/2} \rightarrow 6sp$ excitation have been observed. As reported for other TM compounds,[16,17] this seems to be a general trend associated with the fact that either the corresponding excited state is not available by EELS or the excitation cross section is very low.

The VB region between ~ 4–10 eV of TiO_2 and ZrO_2 has been analyzed by several authors in terms of three Gaussians, in which the high and low BE components involve predominantly bonding and nonbonding orbitals, respectively.[15,16] Such analysis has been also carried out for the spectra of Fig. 1, with three Gaussians centered at 5.35 ± 0.05 eV, 7.00 ± 0.05 eV, and 8.60 ± 0.05 eV, and 2, 1.8, and 2 eV of full width at half maximum, respectively. The CIS curves obtained by this procedure are equivalent to those labeled P1, P2, and P3 in Fig. 3, and therefore they are not shown. It should be pointed out that different resonance behaviors have been found for the bonding and nonbonding components in TiO_2 and ZrO_2.[15,16] However, as observed in Fig. 3, P1, P2, and P3 components show the same resonant behavior, and the resonance enhancement is larger for the low BE feature (P1) than for the high BE features (P2 and P3). This fact should be attributed to the more extended nature of Ta $5d$ and $6sp$ orbitals with respect to Ti $3d$ and Zr

$4d$ orbitals. In fact, the calculated O $2p$, Ta $5d$, and Ta $6sp$ partial DOS are spread out rather uniformly over the whole width of the theoretical VB.[9] Therefore the stronger resonance behavior of the low BE O $2p$ derived states with respect to that of $3d$ and $4d$ TM oxides seems to be mainly associated with the stronger overlap of O $2p$ and Ta $5d$ orbitals.

V. CONCLUSIONS

The electronic structure of stoichiometric and reduced Ta_2O_5 surfaces has been studied by resonant photoemission. The reduced film formed by Ar^+ bombardment of the stoichiometric surface is characterized by the attenuation of the overall VB along with the population of unoccupied Ta derived states in the band gap up to E_F. These changes are attributed to the formation of oxygen vacancies during the reduction of the surface by Ar^+ bombardment. For both stoichiometric and reduced Ta_2O_5 surfaces, constant initial-state curves of the main features of the VB, that is, P1, P2, P3, P4, and P5 at 5.4, 7, 8.6, 3, and 1.6 eV, respectively, show a complex shape with multiple resonance maxima. A satisfactory explanation of these results is achieVed assuming Ta $5p \rightarrow 5d$, $5p \rightarrow 6sp$, and $4f \rightarrow 5d$ photoabsorption mechanisms, and considering the spin-orbit splitting of the Ta $5p$ and Ta $4f$ core levels, and the splitting of the final Ta $5d$ states by crystal-field interactions. In contrast with other $3d$ and $4d$ TM oxides, no differences have been found between the resonant behavior of high BE features (P2 and P3), and low BE features (P1) of the VB. This is attributed to the more extended nature of Ta $5d$ and $6sp$ orbitals with respect to $3d$ and $4d$ cationic orbitals.

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