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# A photoemission study of molybdenum hexacarbonyl adsorption and decomposition on $TiO_2(110)$ surface

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#### Abstract

The adsorption and decomposition of molybdenum hexacarbonyl on (110) TiO<sub>2</sub> surfaces were studied using both core levels and valence band photoemission spectroscopies. It was found that after an adsorption at 140 K, when going back to room temperature, only a small part of molybdenum compounds, previously present at low temperature, remained on the TiO<sub>2</sub> surface. This indicates that the desorption temperature on such a surface is lower than the decomposition one. The use of photon irradiation to decompose the hexa-carbonyl molecule was also studied. It was shown that during such a decomposition molecular fragments were chemisorbed on the surface allowing a higher amount of metal to remain on the surface. It was also shown that it was possible to get rid of adsorbed subcarbonyl groups and to organize the metal atoms by thermal treatments at temperatures as low as 400 K, i.e. much lower than the one needed to obtain the same structures using physical vapour deposition (PVD). Moreover, due to lower used temperatures, this chemical way of deposition allows a better control of the interface than during PVD growth. © 2006 Elsevier B.V. All rights reserved.

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# 1. Introduction

The growth mode of a metal deposited by physical vapour deposition (PVD) technique on a metal oxide substrate often appears hard to control because it is highly related to the interfacial reactivity which is a function of numerous parameters. As concerns to  $Mo/TiO_2(110)$  system, previous works were carried out in order to determine the most relevant parameters playing on both interfacial reactivity and growth mode, these two processes being highly linked [1]. Hence, we successively studied the effects of TiO<sub>2</sub> surface stoichiometry [2], TiO<sub>2</sub> bulk stoichiometry [3], surface roughness [4], molybdenum deposition rate [5], deposited molybdenum amount [6] and subsequent anneal-

ing temperature [3] on the final morphology, crystallinity and stoichiometry of deposits.

The main conclusions were that, for films thicker than a monolayer, the interfacial reaction is less related to the initial state of the substrate (i.e. the initial surface stoichiometry and morphology) than to kinetical parameters such as deposition rate which strongly influences the amount of oxygen atoms which can diffuse into the deposit and the electronic exchanges between metallic molybdenum and titanium ions. Especially, whatever the surface state is and for low enough deposition rate, the interfacial reaction, which occurs at early stage of the deposition, leads to the growth of metastable molybdenum oxide film while both DFT calculations [6] and simple demonstration from macroscopic thermodynamical values [3] show that from a coverage higher than one layer, molybdenum should be metallic. Especially, DFT calculations show that for deposits lower than 1.5 equivalent monolayers (eqML), a special

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organization of molybdenum atoms as pyramidal stripes should occur in the channels delimited by oxygen atom rows which are exhibited along the [001] direction by TiO<sub>2</sub>(110) surfaces [1].

In these special conditions, annealing is thus necessary to break the metastability, i.e. induce the reduction of molybdenum oxide and then lead to equilibrium. However, during such a subsequent annealing, another key parameter plays a major role: the substrate bulk stoichiometry [3]. Indeed, although the film can be fully reduced in the case of an initial non-stoichiometric bulk TiO<sub>2</sub>, the deposit is fully oxidized if the substrate is initially stoichiometric. This fact, which was explained by entropic effect [3], avoids the possibility to make stripes growing on the surface of stoichiometric TiO<sub>2</sub>. Hence, a way to produce molybdenum stripes on stoichiometric surface could be to avoid the initial reaction between the TiO<sub>2</sub> surface and the first deposited molybdenum atoms in order to not have to break metastability through subsequent annealing.

A solution may be deposition of molybdenum at cryogenic temperature in order to kinetically hinder any interfacial reaction. According to this idea, the present study deals with the possibility of depositing molybdenum atoms on TiO<sub>2</sub>(110) surface from a chemical vapour deposition (CVD) route using Mo(CO)<sub>6</sub> as a precursor. Actually this chemical way of deposition has been found to lead to interesting results in catalysts preparation [7–9]. For example Mo nanoparticles prepared using PVD methods are stable on gold surfaces, whereas those prepared using the chemical vapour deposition of a molybdenum hexacarbonyl precursor are found to be mobile, inducing different catalytic properties [10,11].

This paper is about the results concerning the first steps of such a deposition, the precursor adsorption stage and its decomposition.

# 2. Experimental

The  $TiO_2(110)$  sample (MaTeck) was cleaned using the standard procedure which consisted of argon ion bombardments to remove any residual contaminant followed by sample annealing up to 1000 K in ultra high vacuum (UHV). The role of the  $Ar^+$  bombardment was to create defects thanks to the preferential oxygen sputtering; the one of the annealing was to re-organize the sample by diffusion of the defects of the top layers into the whole crystal. In all the experiments presented here, the crystal bulk was under-stoichiometric with a homogenous distribution of defects in the bulk, explaining its blue colour. This deviation from stoichiometry was high enough to allow sample bulk conductivity sufficient to avoid any charging effects during the LEED and photoemission experiments. After annealing, exposures to 100 L of oxygen were done in order to get a fully stoichiometric (110) surface. The quality of the surface was checked with LEED where a sharp  $(1 \times 1)$  LEED pattern with a low background was obtained and with valence band resonance spectra where no contribution of the Ti3d defect band was observed [12].

The Mo(CO)<sub>6</sub> precursor (98%, Aldrich) was held in an independently pumped glass tube at room temperature, which was pumped out for purification. It was then introduced in the vacuum chamber via a micrometric valve to control the pressure (up to  $10^{-5}$  Pa). During exposures, the sample was kept at a temperature around 140 K.

Experiments were carried out on SX700 beamline (bending magnet) at the ASTRID synchrotron source of the Institute for Storage Ring Facilities (Arhus, Denmark). The incident angle of the photon beam and the detection angle were respectively 45° and 0° from the surface normal. The same setup was used for core level spectra (XPS) and valence band spectra (UPS) thanks to a ZEISS SX700 monochromator. Such an apparatus has a wide usable energy range: from 20 to 700 eV. However, the photon beam given by the beamline is not constant over the whole range. Typical flux values for the used settling are ca. 10<sup>10</sup> photons s<sup>-1</sup> at 125 eV and ca.  $10^9$  photons s<sup>-1</sup> at 600 eV. Moreover, the resolution of the SX700 monochromator decreases as the photon energy increases. Because of these reasons, the quality of the spectra decreases with increasing of photon beam energy, which is used for spectrum recording.

For experiments on core level spectra, Ti2p, O1s, C1s and Mo3d, the photon energies were chosen in such a way as to get photoelectrons having almost the same kinetic energies that is to say very close mean free paths and to avoid phantom peaks coming from second order diffraction line through monochromator. Moreover, in order to be as sensitive to surface phenomena as possible, these kinetic energies were chosen between 80 and 100 eV which is the range for the mean free paths minima. Most of valence band spectra were obtained with primary photon energy equal to 45 eV which corresponds to the 3p–3d titanium resonance: thanks to resonance phenomena the sensitivity to Ti3d derived defects is higher for this energy value [12].

The ultrahigh vacuum system with a base pressure of  $7.5 \times 10^{-11}$  mbar was equipped with a quadrupolar mass spectrometer, low energy electron diffraction (LEED) and an electron energy analyser in order to record photoemission spectra. The electron analyser was a VG CLAM II, working with 30 eV pass energy. The energy calibration (Fermi edge) was checked by reference to a metallic molybdenum thick film (>15 nm) which was obtained after molybdenum deposition on TiO<sub>2</sub> substrate using Caburn-MDC e-vap 100 evaporator. The deposition conditions (1.5 eqML min<sup>-1</sup> for 10 min) were specifically chosen to lead to metallic molybdenum film [1]. The sample was put on a Ta foil connected to a copper sample holder that could be cooled down to 140 K with liquid nitrogen or resistively heated up to 1000 K.

## 3. Results and discussion

# 3.1. Exposures

The Mo(CO)<sub>6</sub> exposure experiments at 140 K were analysed first by core level photoemission spectroscopy. Especially, the intensity of Mo(CO)<sub>6</sub> signal (through Mo3d line signal) as well as substrate signal (through Ti2p line signal) was followed as a function of exposure (Fig. 1). It is obvious that the evolution of these signal intensities is best fitted with piecewise-linear variations. Hence, the change of the slopes of the curves recorded for 14 Langmuir exposure can be linked to the end of the filling of the first monolayer and the beginning of the next one in a layer-by-layer growth mode [13]. These experiments prove that molybdenum carbonyl adsorption begins by completion of two monolayers. After adsorption of these two monolayers, the substrate signal intensity begins too low to exhibit a clear behaviour. This point is certainly due to the very low mean free path of detected electrons coming from the substrate (see Section 2). In the same time and for the same reason, the deposit signal intensity changes very slowly because the adsorbed film reached the maximum thickness which can be analysed. After completion of two  $Mo(CO)_6$ monolayers, the rest of the growth can be no longer followed by XPS signal ratio evolution.

In Figs. 2–4 are presented the evolutions of C1s, O1s and Mo3d lines during exposures to molybdenum hexacarbonyl at 140 K up to 25 L in several steps. The corresponding valence band evolution is shown in Fig. 5.

Concerning the C1s lines (Fig. 2), before exposure, no C1s peak is observed, attesting of the absence of carbon contaminants on the sample. After the first exposure to  $Mo(CO)_6$ , a component appears at a binding energy equal to about 288.0 eV. This component increases with increasing  $Mo(CO)_6$  coverage and should thus be attributed to the carbon of the simple physisorbed molecule as shown in a previous study [14]. Another peak, at 5.4 eV higher binding energy, increases in the same way. It can be attributed to shake-up satellite which has been reported for all the carbonyl spectra [14,15]. Besides, shoulder appears on the low binding energy side of the main peak (between 286.6 and 287.6 eV). The appearance of such a shoulder on the



Fig. 1. Evolution of the intensities of the Ti2p and Mo3d lines as a function of  $Mo(CO)_6$  exposure. The dotted line corresponds to the change of the slopes of both curves.



Fig. 2. Evolution of the C1s line during an exposure to  $Mo(CO)_6$  between 0 and 20 Langmuir at 140 K. Primary photon energy: 380 eV.

right part of lines can be attributed to  $Mo(CO)_x$  (x < 6) formation through partial molecule decomposition with CO departure. Such a hypothesis will be more discussed in Section 3.3.

Concerning the O1s spectra (Fig. 3), before exposure, the spectrum is composed of a single line at 530.0 eV which corresponds to the oxygen of the TiO<sub>2</sub> surface. After the first exposure to  $Mo(CO)_6$  another peak appears at around 533.5 eV. As in the case of the peak observed at 288.0 eV in the C1s spectrum, the intensity of this peak increases with increasing  $Mo(CO)_6$  coverage. This peak is related to the oxygen of the  $Mo(CO)_6$  molecule. In the same time, a peak appears at 5.4 eV higher binding energy (shown in Fig. 3 inset) which is characteristic of a shake-up satellite resulting from the same process as the one of the C1s level [14,15].

The photoemission spectra of the Mo3d 5/2 and 3/2 lines are presented in Fig. 4. Although Mo3d lines exhibit a rather wide FWHM which indicates that several molybdenum species are present in the same time at the substrate surface, these lines also exhibit a progressive shift towards higher binding energies during exposures up to ca. 15 L.



Fig. 3. Evolution of the O1s line during an exposure to  $Mo(CO)_6$  between 0 and 25 Langmuir at 140 K. The spectrum in the right hand corner has a larger energy window in order to evidence the satellite peak. Primary photon energy: 600 eV.



Fig. 4. Evolution of the Mo3d line during an exposure to  $Mo(CO)_6$  between 0 and 25 Langmuir at 140 K. Primary photon energy: 320 eV.

For higher exposures, the lines begin to shift in the opposite side that is to lower binding energies. This behaviour should be compared to the fact that 15 L is close to the recorded exposure threshold (14 L) corresponding to completion of the first adsorbed monolayer. Results given by Fig. 4 simply show that different processes occur during completions of the first and the following layers.

The shift recorded during the completion of the first layer is towards higher binding energies. Such a kind of shift is often due to oxidation process of analysed element, which involves the decrease of screening effect around the atoms. The shift recorded after the completion of first monolayer is in the opposite direction and can thus be related to the opposite phenomenon, i.e. molybdenum reduction process. These observations can be interpreted through the electrondonor character of the CO group. If molybdenum hexacarbonyl loses a CO group, it loses also some partial negative charge and it is thus submitted to a kind of oxidation, Mo electrons then being less screened, their binding energies appearing higher. Such a hypothesis can be supported by the appearance of the shoulder on the right part of C1s lines which could also be attributed to  $Mo(CO)_x$  (x < 6) formation through the partial molecule decomposition.

The shift to lower binding energy is observed for exposures beyond 15 L occurs actually after the filling of the first monolayer, i.e. as new adsorbed molecules are no longer in direct contact with TiO<sub>2</sub> surface. Such a second shift seems simply to correspond to the disappearance of the first recorded shift. It could be attributed as the result of adsorption of new non-decomposed Mo(CO)<sub>6</sub> molecules, which hide the ones previously adsorbed and partially decomposed. In these conditions, it seems that partial Mo(CO)<sub>6</sub> molecule decomposition can occur for molecules initially in contact with TiO<sub>2</sub> surface only.

The valence band evolution upon exposure is presented in Fig. 5. The spectrum corresponding to a 200 L exposure is also shown in the same energy range for reference purpose. In this high exposure case, no contribution from both underneath TiO<sub>2</sub> layers and interfacial adsorbed molecules is expected. Hence, the different features can be assigned to



Fig. 5. Evolution of the valence band during an exposure to  $Mo(CO)_6$  between 0 and 25 Langmuir at 140 K. The valence band spectrum obtained after an exposure of 200 L at 140 K is also shown. Primary photon energy: 45 eV.

the components of condensed  $Mo(CO)_6$  without interfacial layer contribution, the partially decomposed molecules seem to be located at the TiO<sub>2</sub> surface only.

Before exposure, the valence band spectrum is composed of the mainly O2p derived band between about 3 and 9 eV, characteristic of stoichiometric TiO<sub>2</sub>, with almost no contribution around 1 eV corresponding to the Ti3d states [12]. Upon deposition, different features appear that the intensities increase with increasing the deposited amount. In the same time, the oxide valence band decreases. A clear assignment can be done for all these peaks by comparison with the 200 L exposure: indeed the spectrum recorded in this case is in good agreement with the ones previously reported in the literature [14]. The feature at 2.4 eV binding energy can be assigned to mainly Mo4d derived molecular orbitals. It should be noticed that this peak exhibits a resonance (not shown here) for photon energies around 49 eV which correspond to the 4p-4d absorption edge [16]. In the binding energy range of 7-10 eV the CO-derived degenerate  $5\sigma - 1\pi$  states are present with the associated satellite at 5.4 eV higher binding energy. At least, the CO  $4\sigma$  level can be observed at a binding energy close to 12 eV. Looking more closely to the feature at the lowest binding energy, i.e. to the one corresponding to Mo4d levels, a shoulder can be observed on the lowest binding energy side of the peak. The presence of this peak is closely related to the shoulder appearing on the C1s and Ols lines (Figs. 2 and 3). These peaks which are at lower binding energies than the main lines come from  $Mo(CO)_x$  $(x \le 6)$  species [17], which should have their origin from the partial decomposition of  $Mo(CO)_6$  [18–22].

## 3.2. Decomposition by thermal treatments

The second step of the experiment was the decomposition of the precursor in order to leave molybdenum on the surface. The sample was thus heated up successively to room temperature (ca. 300 K), and at different temperatures in the 340–820 K range. Such experiments were followed from a sample which was previously exposed to 25 L of Mo(CO)<sub>6</sub> at 140 K. Phenomena are then followed through Mo3d line (Fig. 6), C1s line (Fig. 7), O1s (not shown here) and valence band evolutions. The parts close to the Fermi level only of the latter spectra are shown in Fig. 8.

It can be clearly seen in Fig. 6 showing Mo3d line evolution during annealing, that, at room temperature, only a very small part of molybdenum, previously present at a low temperature, remains on the surface. This indicates that the desorption temperature is lower than the decomposition one. Thus, the molecules of the precursor are slightly bound to the substrate surface and desorb before being decomposed as demonstrated in other cases [18,23]. One should note that different attempts were done to adsorb molecular species at temperatures between 140 and 200 K, but Mo(CO)<sub>6</sub> does not adsorb for temperatures higher than 180 K. After annealing at temperatures higher than 300 K, the Mo3d line exhibits a strong shift to higher



Fig. 6. Evolution of the Mo3d during thermal treatments. The sample was previously exposed to 25 Langmuir of  $Mo(CO)_6$  at 140 K. Primary photon energy: 320 eV.



Fig. 7. Evolution of the C1s during thermal treatments. The sample was previously exposed to 25 Langmuir of  $Mo(CO)_6$  at 140 K. Primary photon energy: 380 eV.



Fig. 8. Evolution of the low binding energy part of the valence band during thermal treatments. The sample was previously exposed to 25 Langmuir of  $Mo(CO)_6$  at 140 K. Primary photon energy: 45 eV.

binding energies during the annealing. Using the whole of our previous results on Mo/TiO<sub>2</sub> system [1] as spectroscopic fingerprint for the Mo3d core level, one can suppose that after annealing the deposits correspond to oxidized molybdenum species  $MoO_x$  with x < 2.

As concerns the evolution of C1s lines (Fig. 7), the only components, which remains in a very small amount on the surface after the return to room temperature, are those corresponding to  $Mo(CO)_x$  species. This confirms that  $Mo(CO)_6$  completely desorbs and/or is decomposed during the heating up to room temperature. However, the intensity of the C1s component related to  $Mo(CO)_x$  (x < 6) species does not really increase during return to room temperature. This point seems to indicate that there is no additional  $Mo(CO)_6$  decomposition phenomenon during heating up to room temperature. In other words, during annealing,  $Mo(CO)_6$  simply desorbs and the presence of a small amount of molybdenum on the TiO<sub>2</sub> surface after return at room temperature is to be related to the presence, before subsequent annealing, of  $Mo(CO)_x$  (x < 6).

In order to get rid of the carbon-based species remaining on the surface, the samples were submitted to subsequent annealings at different temperatures in the 340-820 K range. It should be observed that, after an annealing at 340 K, all the molybdenum subcarbonyl species observed at room temperature disappeared but there is still some remaining adsorbed carbon on the surface at a binding energy around 284.9 eV (Fig. 7). This carbon line is comparable (energy, intensity) to the one obtained after the already used deposition method (physical vapour deposition, PVD) for the same deposited molybdenum amount. Thus, it can be concluded that carbon observed after an annealing at 340 K corresponds to a kind of adventitious carbon adsorbed on the surface as it is often the case in UHV experiments even in the case of oxide systems. So, this proves that, even though the Mo deposition method using molybdenum hexacarbonyl as precursor introduces some carbon, a subsequent annealing at quite a low temperature induces the desorption from the surface of all the carbon species carried by the hexacarbonyl: after such an annealing, just

adventitious carbon is detected by photoemission. It should also be noticed that no molybdenum carbide species are present on the surface after annealings in opposition with other studies carried out on the alumina substrate [24].

The evolution of the part closest to the Fermi level of the valence band (Fig. 8) during annealing is remarkable: the global intensity of the line recorded in the  $TiO_2$  gap strongly decreases and just a component is detectable in this line when the sample was at room temperature. This single component can be attributed to Mo4d states, low but detectable molybdenum amount remaining at the surface. Moreover, such a component appears at the same energy like the component which was due to Mo in  $Mo(CO)_x$  $(x \le 6)$ . The one which was due to Mo in Mo(CO)<sub>6</sub> actually completely disappeared after going back to room temperature. After annealing at higher temperature, drastic changes can be observed in the valence band region, the peak recorded at room temperature disappeared while a new component at about 0.8 eV appears. This line is very similar to the one recorded for fractional Mo deposits [6] carried out by the PVD method. In such a case, the peak close to the Fermi level corresponds to Ti3d states due to interaction between deposited molybdenum and TiO<sub>2</sub> surface, molybdenum being oxidized whereas titanium is reduced. A similar phenomenon seems to occur here. After  $Mo(CO)_x$  (x < 6) decomposition, molybdenum is free to react with substrate and this seems to begin from 340 K.

The data recorded on valence band are in agreement with the ones recorded on Mo3d line: after annealing, i.e. after total carbonyl species decomposition, the low amount of molybdenum remaining at the surface reacts with TiO<sub>2</sub> giving molybdenum oxide as well as reduction of titanium. However, although it seems possible, using the decomposition of molybdenum hexacarbonyl by thermal treatments to get rid of carbonyl species and to obtain molybdenum oxide, the final deposited molybdenum amount is very low. Besides, a noticeable point is the fact that whatever the initial molybdenum hexacarbonyl exposure is, the molybdenum amounts remaining at the surface is always in the same fractional monolayer range. According to this, it seemed to us that the key point was the balance between the  $Mo(CO)_6$  decomposition and desorption. Indeed, the precursor amount which is not decomposed at cryogenic temperature seems to simply desorb during annealing, the remaining molybdenum amount being related to the formation of subcarbonyl species at the early stage of the deposition.

#### 3.3. Decomposition by photon irradiation

In order to decompose the molybdenum hexacarbonyl precursor in a more efficient way before annealing, i.e. before desorption of these molecules, attempts were done of irradiating the sample with photons after the adsorption step. Indeed this kind of procedure has been shown to be efficient for Mo deposition on different metallic [25–29] surfaces.



Fig. 9. Evolution of the low binding energy part of the valence band during an irradiation to the zero-order light. An exposure of 25 Langmuir  $Mo(CO)_6$  at 140 K was performed before irradiating. Primary photon energy: 45 eV.



Fig. 10. Evolution of the C1s line during an irradiation to the zero-order light. An exposure of 25 Langmuir of  $Mo(CO)_6$  at 140 K was performed before irradiating. Primary photon energy: 380 eV.

Attempts of irradiating the sample with photons were simply done using photons provided by the zero-order beam of the synchrotron radiation. This was followed mainly from the evolutions of the valence band (Fig. 9) as well as C1s line (Fig. 10) on a sample previously exposed to 25 L Mo(CO)<sub>6</sub> at 140 K.

The evolution of the low binding energy part of the valence band upon irradiation of such a sample is shown in Fig. 9. It can be seen in this figure that the shape of the line previously attributed to Mo4d derived molecular is modified upon irradiation while its average binding energy is strongly shifted to lower binding energies: a 0.3 eV shift is evidenced after only 30 s of irradiation and it increases up to 1.3 eV after the longest irradiation. Actually, the appearance of such a broad and shifted line may be related to the partial decomposition of the precursor, which is more and more important upon irradiations.

This hypothesis is evidenced in the C1s (Fig. 10) and O1s lines (not shown here) where both the peaks attributed to

Mo(CO)<sub>6</sub> and to its satellites decrease and shift to lower binding energies upon irradiation because of decomposition to subcarbonyl species. Especially, after 25 min of irradiation, no Mo(CO)<sub>6</sub> species is not observable on the C1s spectrum as shown in Fig. 10 and just Mo(CO)<sub>x</sub> (x < 6) species can be detected.

Moreover, after 25 min of irradiation, the main component of the O1s line (not shown here) is clearly the one at 530.0 eV corresponding to the oxygen of the TiO<sub>2</sub> surface. This point is in agreement with the  $Mo(CO)_6$  decomposition which leads to CO departure i.e. a decrease of the CO component intensity of O1s line. In the same time, because CO molecules leave the surface, the substrate is less hidden by adsorbed molecules and the intensity of TiO<sub>2</sub> component of O1s line increases.

Besides, after subsequent annealing at 420 K, no more CO component of O1s line is observed while the C1s spectrum exhibits only one component related to adventitious carbon species (Fig. 10). These observations prove that after a mild annealing, the carbonyl decomposition and/ or desorption is completed. However, after such treatments, one can note that a lot of molybdenum remains on the TiO<sub>2</sub> surface as shown in Fig. 11e. This indicates that in such a case the decomposition phenomenon dominate the desorption one. Hence, it seems that after partial  $Mo(CO)_6$  decomposition, subcarbonyl species cannot desorb during annealing, but should decompose. A simple explanation of this phenomenon can be the change of bounds between molecules and substrate as molybdenum carbonyl is decomposed. In other words, although  $Mo(CO)_6$  is slightly bound to the surface,  $Mo(CO)_x$ (x < 6) is stuck to the TiO<sub>2</sub> surface through a real chemical bound, which avoids desorption during annealing and then leads to a complete decomposition of the precursor.

A strong photon irradiation of the sample at cryogenic temperature is thus an efficient way to make leaving molyb-



Fig. 11. Comparison of the Mo3d spectra as a function of the deposited Mo amount. The spectra were all obtained after an annealing at 420 K. Spectrum (a) was obtained after an exposure of 10 Langmuir Mo(CO)<sub>6</sub> at 140 K without subsequent zero-order irradiation; Spectrum (b) was obtained after an exposure of 10 Langmuir Mo(CO)<sub>6</sub> at 140 K with subsequent zero-order irradiation for 30 s; other spectra were obtained after an exposure of 10 (c), 15 (d) and 25 (e) Langmuir of Mo(CO)<sub>6</sub> at 140 K followed by zero-order irradiation for 25 min. Primary photon energy: 320 eV.

denum on the substrate surface. It should be noticed that, in the range of photons energies we were able to use (from about 30 to 650 eV) no real influence of the excitation energy on the precursor decomposition was observed: only the photon dose seems to play a role. This should certainly not be the same using irradiations in the UV-range, closer to the maximum in the adsorption spectrum of  $Mo(CO)_6$ [30], but unfortunately SX700 beamline does not allow to reach such an energy range.

It should also be noticed that each spectrum recording implies irradiation of the sample and then induces low but a noticeable decomposition of the precursor as evidenced in Figs. 9 and 10: after acquisition of some spectra, shoulders which appeared on the right part of lines noticeably increased proving additional  $Mo(CO)_x$  (x < 6) formation. Such a decomposition can explain why a low amount of Mo can remain on the TiO<sub>2</sub> surface after going back to room temperature even without specific zero-order irradiation. Irradiation by the photon beam needed to record spectra used to follow the reaction steps is enough to initiate  $Mo(CO)_6$  decomposition. Actually, the decomposition phenomenon revealed during the first adsorbed layer is probably mainly due to spectrum recording. Indeed, in this case, the adsorbed molecule amount is low (lower than one monolayer) and the photon irradiation spent a long time (several spectra were recorded for each adsorption step). Moreover, for a same adsorption step, the precursor decomposition is lower after the recording of the first spectrum than after the recording of the last one, i.e. after that the sample was irradiated for a long time (see Section 3.1). This fact can explain why the decomposition is more revealed by a specific spectrum rather than by another one. For instance, after an exposure of 15 L Mo(CO)<sub>6</sub>, the decomposition is less revealed by Mo4d additional component in the valence band spectrum (Fig. 5) than by the shift of the Mo3d lines towards higher binding energies (Fig. 4). In such a case, valence band spectrum was recorded just after adsorption, whereas Mo3d spectrum was recorded afterwards.

Fig. 11 shows the Mo3d lines of some depositions carried out from some  $Mo(CO)_6$  exposures with or without zero-order irradiation. In this figure, it is clear that the amount of molybdenum remaining at the substrate surface is related to both exposition and irradiation. Moreover, the binding energies of the Mo3d lines are functions of the remaining molybdenum amount. For instance, the Mo3d lines corresponding to the highest deposited Mo amount is characterized by the binding energy of Mo3d5/2 line equal to 227.8 eV (Fig. 11e). The valence band related to the same sample is characterized by the states at the Fermi level (see the topmost curve of Fig. 9). These two observations are in a good agreement with metallic molybdenum. In the contrary, lowest deposits are characterized by a Mo3d5/2 line binding energy in the 228.8–228.0 eV range. Such a phenomenon can be explained by metallic clusters having a very low size which then induces a less efficient screening during photoemission process and thus a shift



Fig. 12. Ti2p spectra for the TiO<sub>2</sub> surface before (doted line) and after (solid line) molybdenum deposition. The deposition was carried out from an exposure of 10 Langmuir of  $Mo(CO)_6$  at 140 K with subsequent zero-order irradiation for 30 s followed by an annealing at 420 K. Primary photon energy: 510 eV.

of lines towards higher binding energies [31]. However, if such a phenomenon can induce significant shifts [32], these ones are always lower than 1 eV whereas the one record here can reach this value. Moreover, the Mo3d shift occurs at the same time as Ti2p spectrum change (Fig. 12). Indeed, in Ti2p spectrum, after the deposition of a low amount of molybdenum followed by an annealing at 420 K, additional component clearly appears on the right part of Ti2p3/2 line. Such an additional component is well known [34] and corresponds to the titanium reduction. The Mo3d line shift should thus be due to concomitant molybdenum oxidation. In the case of low molybdenum deposits, molybdenum oxide phases seem thus to be formed.

Similar conclusions were obtained from the deposits performed by the PVD method [33] after annealing at 673 K. Hence, it seems that molybdenum phases formed by decomposition of  $Mo(CO)_6$  followed by a subsequent annealing at 420 K and those obtained by classical PVD deposition followed thermal treatments are chemically pretty close. However, in our previous studies upon the growth mode of Mo deposited on TiO<sub>2</sub> by PVD technique, one of the main conclusions was that, for films thicker than one monolayer, the interfacial reaction is less related to the initial surface stoichiometry and morphology than to kinetical parameters such as, for instance, deposition rate. A consequence of this fact is that metastable state occurs during PVD deposition at room temperature and that annealing step (at 673 K) is necessary to reach a kind of equilibrium [33]. In the case of Mo deposition using  $Mo(CO)_6$ , any influence of deposition rate is suppressed because the first step of the protocol is always the adsorption of the precursor and is well separated from the second one, i.e. the decomposition. Thus, this method allows to reach the equilibrium after annealing at temperature as low as 420 K only, this temperature being efficient to totally decomposed the precursor. The proposed deposition technique allows thus to perform stable molybdenum structures at lower temperature than by the PVD method. For example, the highest deposit performed during this study is metallic (characterized by the binding energy of

## 4. Conclusion

It was shown that it is possible, using the decomposition of molybdenum hexacarbonyl followed by thermal treatments to obtain molybdenum based phases and to get rid of carbon species. However, although simple annealing allows to obtain molybdenum amounts in the submonolayer range, one should note that the remaining Mo amount should be related to photon irradiation occurring during the recording of spectra which initiates the decomposition of a low part of the adsorbed precursor molecules. To obtain higher deposits, sample irradiations by a photon beam can be used.

Moreover, using this kind of precursor decomposition and annealing at 420 K, the same kind of Mo nanostructures can be formed on the surface as after PVD followed by thermal treatments at much higher temperatures. One of the interests of the method using Mo(CO)<sub>6</sub> comes thus from the annealing temperature needed to obtain the final molybdenum phases. Actually, like for many metals deposited on oxides, some diffusion phenomena between the substrate and the deposit may occur upon annealing, changing the final deposit state. In the case of PVD deposited molybdenum, an annealing at temperatures in the 700 K range, which is the one needed to obtain some specific phases, should induce the diffusion of oxygen from the bulk to the deposit leading to the formation of molybdenum oxide instead of the desired structures [1,3]. On the contrary, in the method using molybdenum hexacarbonyl decomposition, the needed temperatures are rather low and thus prevent any bulk diffusion phenomena.

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