



First nucleation steps of vanadium oxide thin films studied by XPS inelastic peak shape analysis

F. Gracia*, F. Yubero, J.P. Espinós, A.R. González-Elipe

Instituto de Ciencia de Materiales de Sevilla (CSIC–U. Sevilla) and Dpt. Q. Inorgánica, c/Américo Vespucio s/n, E-41092 Sevilla, Spain

Available online 15 August 2005

Abstract

The initial states of deposition of vanadium oxide thin films have been studied by analysis of the peak shape (both inelastic background and elastic contributions) of X-ray photoemission spectra (XPS) after successive deposition experiments. This study has permitted to assess the type of nucleation and growth mechanisms of the films. The experiments have been carried out in situ in the preparation chamber of a XPS spectrometer. Thin films of vanadium oxide have been prepared on Al_2O_3 and TiO_2 by means of thermal evaporation, ion beam assisted deposition and plasma enhanced chemical vapour deposition. The thin films prepared by the first two procedures consisted of V_2O_4 , while those prepared by the latter had a V_2O_5 stoichiometry. The analysis of the inelastic background of the photoemission spectra has shown that the films prepared by thermal evaporation on Al_2O_3 are formed by big particles that only cover completely the surface of the substrate when their height reaches 16 nm. By contrast, the thin films prepared with assistance of ions on Al_2O_3 or with plasma on TiO_2 consist of smaller particles that succeed in covering the substrate surface already for a height of approximately 4 nm. Thin films prepared by plasma-assisted deposition on Al_2O_3 depict an intermediate situation where the substrate is completely covered when the particles have a height of approximately 6 nm. The type of substrates, differences in the deposition procedure or the activation of the adatoms by ion bombardment are some of the factors that are accounted for by to explain the different observed behaviours.

© 2005 Published by Elsevier B.V.

PACS: 82.80.P; 81.15

Keywords: XPS; Thin film; Growth mechanism; Vanadium oxide; Nucleation; XPS background analysis

1. Introduction

Determination of the growing mechanism of thin films is of the outmost importance for the control of

their microstructure and, therefore, final properties and performance under operation. In this context, the initial stages of growth of thin films (i.e., first nucleation steps) are critical because they determine the evolution of the microstructure of the film when it grows in thickness [1]. Typically, the initial stages of growth of thin films have been analysed directly by

* Corresponding author.

E-mail address: torres@icmse.isic.es (F. Gracia).

transmission electron microscopy (TEM) or scanning electron microscopy (SEM) [2] and, more recently, atomic force microscopy (AFM) and similar probes [3,4]. However, depending on the system, the use of these methods may have important limitations. This is particularly evident when the materials of the substrate and deposited layer do not permit a clear differentiation by electron microscopy (e.g., two oxides of similar electron density) or when the substrate is relatively rough and the first deposited particles cannot be differentiated by AFM. On the other hand, for flat substrates and single crystals, the analysis of the initial stages of growth of thin films up to a few monolayers can be carried out by comparing the relative intensities of the peaks of substrate and deposited layers. With this type of substrates, this procedure can be used for thickness up to a few equivalent monolayers and permits to check whether the film grows according to a layer by layer or an island formation mechanism [5,6]. In the present paper, dealing with the analysis of the growth mechanism of vanadium oxide thin films deposited on Al_2O_3 and TiO_2 substrates, we propose to analyse the shape of the photoemission spectra according to the Tougaard procedure to determine the size of the first nuclei of the deposited films [7,8]. In a previous publication, we have reported the use of this procedure to describe the size and shape of ZnO and tin oxide nuclei grown on alumina substrates [9,10].

Vanadium oxide thin films are very useful materials for many applications as catalysts, layers that change its colour around room temperature, electrodes in electrochromic coatings, etc. [11,12]. For any of these applications, the microstructure of the films plays a critical role and is determined by both the characteristics of the substrate and the type of procedure that is used for the synthesis of the films. In the present work, we address these two issues by comparing the results obtained for vanadium oxide thin films grown on TiO_2 and Al_2O_3 by using three different procedures of synthesis: plasma enhanced chemical vapour deposition (PECVD), thermal evaporation and ion beam assisted deposition (IBAD). The obtained results have shown that depending on the substrate and the preparation procedure, the size of the first nuclei and the ability to cover the substrate (wetting) drastically change. Moreover, it has been also found that the oxidation state of vanadium is different

according to the preparation procedure, obtaining V_2O_4 for thermal evaporation and IBAD methods or V_2O_5 for PECVD.

2. Experimental

Vanadium oxide thin films have been deposited on Al_2O_3 and TiO_2 substrates in the preparation chamber of an X-ray photoemission spectrometer. They were analysed in situ by X-ray photoemission spectroscopy (XPS) for increasing times of deposition. The substrates consisted of compact thin films of these two materials or optically polished sapphire and single crystals of TiO_2 . The substrates were cleaned in situ by a mild bombardment with O_2^+ ions of 1000 eV kinetic energy. Thin films were grown by thermal evaporation, PECVD and IBAD procedures. Thermal evaporation was carried out by heating resistively a tungsten wire with a spring shape where a piece of metallic vanadium was placed. Evaporation was done under a partial pressure of $\sim 10^{-5}$ Torr of oxygen for increasing intervals of time. The samples were analysed after each deposition. The IBAD deposition was done with the same experimental set-up than before, but by subjecting the substrates to ion bombardment while the film was growing. Bombardment was done with an ion gun working with oxygen (i.e., O_2^+ ions) and providing ions of 500 eV of kinetic energy. An ion current density of approximately $5 \mu\text{A cm}^{-2}$ was used while the evaporation rate was adjusted to compensate the sputtering removal of the deposited layer. The partial pressure of oxygen during this IBAD deposition experiment was 2×10^{-6} Torr. The PECVD deposition of the film was also done “in-situ” by using a very simple plasma source consisting of a quartz tube fed with oxygen (2×10^{-2} Torr). Plasma was activated with a MW (2.45 GHz) cavity working at a power of 50 W. The plasma was directed towards the surface of the substrate (i.e., downstream configuration) while the precursor (VOCl_3) was dosed on its surface. Partial pressures of the precursor and oxygen were 2×10^{-5} and 2×10^{-2} Torr, respectively. All the experiments were done at room temperature.

XPS spectra were recorded after each deposition step with a VG ESCALAB210 spectrometer working in the pass energy constant mode with a pass energy of

50 eV. The Mg K α radiation was used for excitation of the spectra, while the calibration of the binding energy scale was done by adjustment with the Ti 2p or Al 2p peaks of the substrates.

For the XPS background analysis, V 2s of the deposited oxide and the Ti 2p photoemission peak and the Al *KLL* Auger peak of the substrates were recorded. The background behind the elastic peak varied from approximately 80/100 eV for the V 2s and Al *KLL* peaks to 60 eV for the Ti 2p. The spectra were analysed using the QUASES software package [13].

3. Results

Fig. 1 shows a series of V 2p and O 1s photoemission spectra for vanadium oxide deposited by thermal evaporation on Al₂O₃ for increasing periods of time. These spectra clearly evidence that for increasing evaporation times the intensity of the V

2p peak increases while the position and shape of the O 1s peak vary (the O 1s peak position shifts from 531.2 to 530.5 eV). Meanwhile, the binding energy (BE) of the V 2p_{3/2} peak was 517.0 eV for the first deposition experiment and then varied to 516.4 eV for the rest of depositions. These values are characteristic of V⁴⁺ species [14] and, therefore, we assume that under these experimental conditions we are forming V₂O₄ particles. Shifts in the BE of photoemission peaks of small oxide particles deposited on another oxide substrate are a very common phenomenon that have been discussed by us in much detail in previous works [15]. Similar results were obtained for the other experiments. The most significant difference between the results of the PECVD and those of IBAD and thermal evaporation experiments is that the BE of the V 2p_{3/2} peak in the former case is between 517.4 and 517.6 eV depending of the substrate. This BE is typical of V⁵⁺ species and shows that with PECVD the deposited thin films consist of V₂O₅. This difference is interesting because most results in literature dealing with the deposition of very thin films of vanadium oxide on Al₂O₃ or TiO₂ substrates to model the situation in V₂O₅/Al₂O₃ and V₂O₅/TiO₂ catalysts report the formation of V⁴⁺ species [16,17].

The analysis of the photoelectron peak shapes including the background behind the photoemission peaks according to the Tougaard's method [7,8] provides an easy way of accounting for the type of growth mode (i.e., layer by layer or islands) and the size and shape of the particles when three dimensional particles form on the surface of the substrate. Fig. 2 shows, as an example, the evolution of the Ti 2p spectra for vanadium oxide deposited on TiO₂ by PECVD for increasing periods of time. These spectra clearly show that the intensity ratio between the elastic peak and the inelastic background decreases as the amount of deposited V₂O₅ increases. From the analysis of these spectra by means of the QUASES software [13] program, it is possible to determine, for each deposition experiment, the height of the particles and the fraction of the surface of substrate that is covered by the deposited film. It is important to mention here that for this analysis to be reliable it is necessary that there is a noticeable change in the height and shape of the background. This makes that this analysis can only be applied when there is already a certain amount of deposited material and therefore, it

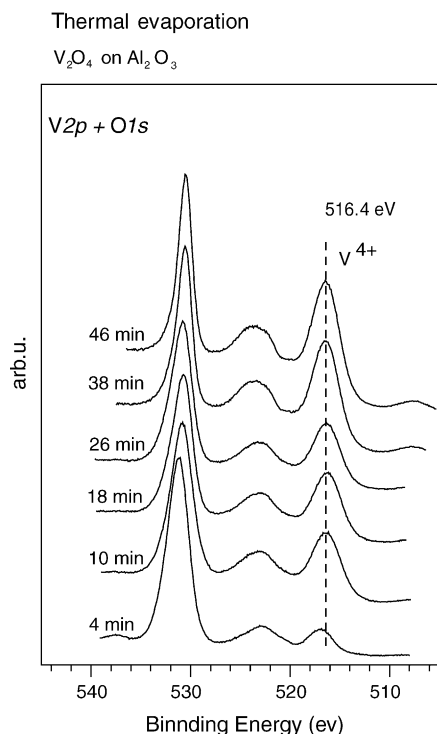


Fig. 1. V 2p and O 1s spectra for vanadium oxide deposited by thermal evaporation on the surface of Al₂O₃ for increasing periods of time.

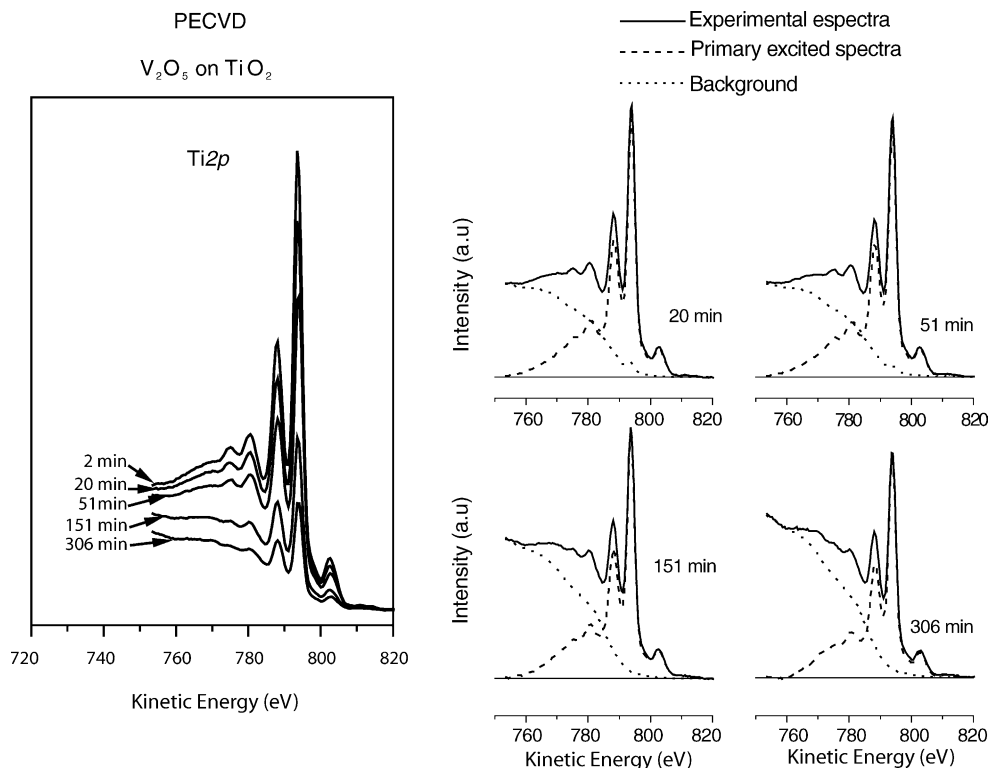


Fig. 2. (Left) Ti 2p spectra used to perform XPS inelastic peak shape analysis with QUASES software. The spectra correspond to the deposition of vanadium oxide on TiO_2 by PECVD for the indicated periods of time. (Right) Curves corresponding to the experimental spectra, calculated background and primary excited spectra are reported.

is not very sensitive for amounts of the order of one equivalent monolayer.

The results of analysis of this kind are reported in Figs. 3 and 4 for the different systems studied. For this analysis, a growing profile described by an average island height h and a surface coverage c is assumed. Fig. 3 (left) shows the results corresponding to the thermal and IBA deposition on Al_2O_3 . For the thermal evaporation case, this figure shows that at the beginning of the deposition (after 4 min evaporation) there is a 40% of the substrate surface covered by very small particles of ~ 1 nm height. Successive evaporations contribute to increase significantly the height h of the particles (i.e., 7 nm height for 18 min evaporation) although the surface coverage c remains almost inalterable (i.e., 50% for 18 min evaporation). Only after evaporation for longer times (i.e., 38 and 46 min), the extent of covered surface increases up to 80–100% coverage, although for these times the

height of the particles is already between 14 and 16 nm. To assess the amount of material that is deposited in each case in Fig. 3, they have been represented a series of dashed curves which are calculated by making the product $c \times h = \text{AOS}$. Thus, AOS is the amount of deposited substance, which in the figures, is specified for each dashed line.

Analyses similar to that reported in Fig. 3 (left) have been also carried out for the other experimental situations. However, in these other cases, calculations have been made under two assumptions: by assuming a homogeneous distribution of island heights (i.e., fixed particle size as in the previous analysis shown in Fig. 3 (left)) or an exponential distribution of island heights. In this latter case, the parameters that define the profile are the surface coverage and the characteristic length of the exponential distribution L of heights [7,8,13]. The obtained curves for the other three experimental

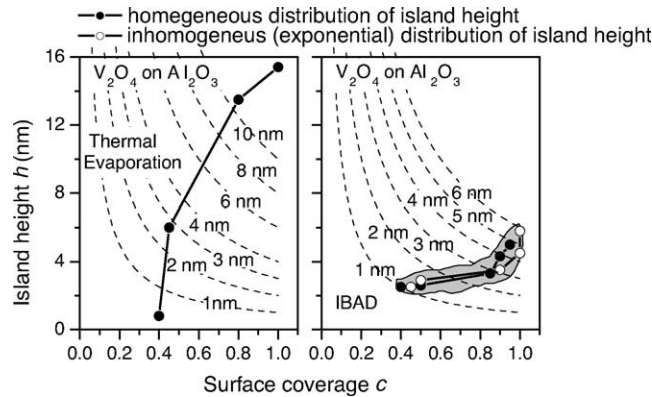


Fig. 3. (Left) Plot of the island height against the surface coverage for vanadium oxide deposited on Al_2O_3 by thermal evaporation for 4, 18, 38 and 46 min and (right) by IBAD for 7, 17, 25 and 35 min. Results are represented for calculations under the assumption of homogeneous size of the particles (●) and an exponential distribution of island heights, i.e., an inhomogeneous distribution of particle size (○). The dashed lines represent fixed AOS, as indicated (see text).

situations are reported in Fig. 3 (right) and Fig. 4 (left and right).

The comparison of the shape of these curves with that of Fig. 3 (left) reveals clear differences. In general, a high surface coverage is obtained with particles of a maximum height of ~ 4 nm (Fig. 3 (right) and Fig. 4 (right)). Fig. 4 (left) shows the evolution of V_2O_5 films prepared by PECVD on Al_2O_3 as substrate. In this situation particles as high as ~ 6 nm are formed for full surface coverage. It is also interesting from the curves in these figures that, except for the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ system prepared by PECVD (Fig. 4 left), the results

are rather similar by assuming that the particles are homogeneous in size or that they follow an exponential distribution function.

4. Discussion

First evidence from the previous results is that, depending on the preparation procedure of the thin films, either V_2O_4 or V_2O_5 are obtained. This is interesting to model the behaviour of $\text{V}_2\text{O}_x/\text{MO}_y$ systems, a subject of the outmost interest for the

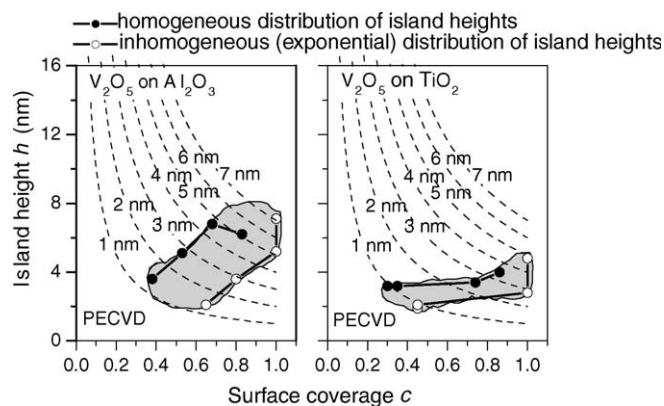


Fig. 4. (Left) Plot of the island height against the surface coverage for vanadium oxide deposited by PECVD on Al_2O_3 for 20, 51, 156 and 306 min (left) and (right) TiO_2 for 20, 51, 151 and 306 min. Results are represented for calculations under the assumption of homogeneous size of the particles (●) and an exponential distribution of island heights, i.e., an inhomogeneous distribution of particle size (○). The dashed lines represent fixed AOS, as indicated (see text).

surface science community and where very often only the formation of V_2O_5 has been reported [16,17]. Second evidence refers to the growing mechanism of the thin films. Starting from the situation outlined in Fig. 3 (left) (thermal evaporation of V_2O_4 on Al_2O_3), this is consistent with a columnar growth mechanism, a classical behaviour of thin films prepared by evaporation when no extra energy is supplied by heating or any other means. The curve in Fig. 3 (left) clearly shows that for the first deposition steps a series of small particles are formed. These particles grow in height and much less in width, making possible that only for particles as height as ~ 16 nm full coverage of the substrate is achieved. When the growth of the thin film is assisted by ion bombardment (IBAD procedure), the situation is completely different and it appears that the particles grow less in height and cover first the surface (note however, that with the background analysis procedure we cannot differentiate between a situation consisting of a limited number of wide particles and another with a high number of particles with similar height and width). This makes that total coverage of the surface is achieved with particles with a height of ~ 4 nm. The difference in growth mechanism between thermally evaporated and IBAD thin films can be justified by considering the extra energy supplied to the system by the impinging ions arriving to the thin films. This energy activates the surface and provides much mobility to the adsorbed adatoms which, in this way, move over the surface and can eventually form another nuclei up to achieve total coverage [18].

The results in Fig. 4 correspond to V_2O_5 thin films prepared by PECVD. Compared with the evaporated thin films, it is apparent that surface wetting with vanadium oxide is easier here. It is likely that this is related with the type of growing process involved. The PECVD system used in this experiment works under a “downstream configuration”. This means that plasma species react on the surface with adsorbed molecules of the precursor. It is likely that the mobility of the adsorbed molecules of precursor on the surface of both Al_2O_3 and TiO_2 is higher than that of metal or oxide molecules or moieties. In this way, it is reasonable that the coverage of the substrate occurs more easily by PECVD than by thermal evaporation. Nonetheless, it is also interesting that, under completely equivalent conditions, V_2O_5 spread more easily on TiO_2 than on

Al_2O_3 . We tend to explain this feature by claiming that the interface tension must be smaller on titanium oxide. This feature is well documented in the field of catalysts where the V_2O_5/TiO_2 catalysts used for selective reduction of NO with NH_3 , selective oxidation of hydrocarbons and other applications are characterized by a very good dispersion of the V_2O_5 on the surface of anatase [19].

A final remark concerns the difference in particle sizes obtained by considering in the calculations either a homogeneous distribution or an exponential one for the island heights. For the V_2O_5/Al_2O_3 system prepared by PECVD, there is significant difference in the obtained particle sizes. At this stage, it is difficult to decide which of the two models, homogeneous or exponential distributions, is closer to the actual situation of the sample. For a deposition experiment carried out at room temperature, this latter seems more realistic and we believe this must be the option of choice in this case.

5. Conclusions

The previous results and discussions clearly prove that XPS background analysis can be used to assess the type of growing mechanism of thin films. This method can be specially advisable when the substrate and thin film materials have similar electron densities and when the substrate is relatively rough. In this work, we have analysed the case consisting of vanadium oxide thin films prepared by three different preparation procedures (thermal evaporation, IBAD and PECVD). The obtained results, i.e., a columnar growth for evaporated films, and more flat and compact layers for IBAD and PECVD films, are consistent with the microstructures that are expected for these types of preparation procedures. In this respect, it is particularly interesting the situation for the IBAD films in comparison with the evaporated ones, where the spreading of the film can be related with the extra energy supplied to the surface by the accelerated ions impinging onto the surface [18].

Acknowledgment

We thank the Spanish Ministry of Science and Education (MAT2004-01558) for financial support.

References

- [1] L. Pranevicius, *Thin Solid Films* 63 (1979) 77.
- [2] J.C. Arnault, J. Delafond, C. Templier, J. Chaumont, O. Enea, *Nucl. Instrum. Methods Phys. Res. Sect. B* 81 (1993) 1384.
- [3] P.H. Bolt, E. Ten Grotenhuis, J.W. Geus, F.H.P.M. Habraken, *Surf. Sci.* 329 (1995) 227.
- [4] H. Brune, *Surf. Sci. Rep.* 31 (1998) 121.
- [5] V.M. Jiménez, J.P. Espinós, A.R. González-Elipe, *Surf. Interface Anal.* 26 (1998) 62.
- [6] Ch.T. Campbell, *Surf. Sci. Rep.* 27 (1997) 1.
- [7] S. Tougaard, *J. Vac. Sci. Technol. A* 14 (1996) 1415.
- [8] S. Tougaard, *Surf. Interface Anal.* 26 (1998) 249.
- [9] A.I. Martín-Concepcion, F. Yubero, J.P. Espinos, A.R. González-Elipe, S. Tougaard, *J. Vac. Sci. Technol. A* 21 (2003) 1393.
- [10] R. Reiche, S. Oswald, F. Yubero, J.P. Espinos, J.P. Holgado, A.R. Gonzalez-Elipe, *J. Phys. Chem. B* 108 (2004) 9905.
- [11] C. Martin, V. Rives, V. Sanchez-Escribano, G. Busca, V. Lorenzelli, J. Ramis, *Surf. Sci.* 251/252 (1991) 825.
- [12] M.S. Burdis, *Thin Solid Films* 311 (1997) 286.
- [13] S. Tougaard, QUASES, Software package for quantitative XPS/AES of surface nanostructures by inelastic peak shape analysis, www.QUASES.com.
- [14] M. Sambì, J. Sangiovanni, G. Granozzi, *Phys. Rev. B* 55 (1977) 7850.
- [15] A.R. González-Elipe, F. Yubero, Spectroscopic characterization of oxide/oxide interfaces, in: H.S. Nalva (Ed.), *Handbook of Surface and Interfaces of Materials*, vol. 2, Academic Press, San Diego, 2001, p. 147.
- [16] Q. Wang, R.J. Madix, *Surf. Sci.* 474 (2001) 213.
- [17] K. Devriendt, H. Poelman, L. Fiermans, *Surf. Interface Anal.* 29 (2000) 139.
- [18] A.R. Gonzalez-Elipe, F. Yubero, J.M. Sanz, *Low Energy Ion Assisted Film Growth*, Imperial College Press, London, 2003.
- [19] K. Debriendt, H. Poelman, L. Fiermans, *Surf. Interface Anal.* 29 (2000) 139.