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2005 J. Phys.: Condens. Matter 17 6813

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# High-resolution photoelectron spectroscopy studies on WO<sub>3</sub> films modified by Ag addition

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Received 24 July 2005, in final form 25 September 2005

Published 14 October 2005

Online at [stacks.iop.org/JPhysCM/17/6813](http://stacks.iop.org/JPhysCM/17/6813)

## Abstract

In this work, WO<sub>3</sub> films loaded with different amounts of Ag atoms, prepared by screen-printing onto Si substrates and annealed in air at 300 and 600 °C, were investigated. Atomic force microscopy micrographs showed that the films are nano-particulate with increasing final grain size on increasing the annealing temperature and/or Ag loading level. The observation of a Raman band near 930 cm<sup>-1</sup>, whose intensity increased on increasing the level of Ag loading for the samples annealed at 600 °C, suggests the intercalation of Ag into WO<sub>3</sub> tunnels; this is supported by the presence of a peak at 32 eV binding energy in the high-resolution x-ray photoelectron (XP) spectra. From the analysis of the W 4f core level XP spectra it was also observed that when the level of Ag loading increases, the component in the spectra associated to surface defects decreased; as the measured concentration of Ag in the films is 1.8 higher than the nominal one when the samples are annealed at 600 °C, the XPS observations strongly suggest that the Ag atoms migrate to the surface of the WO<sub>3</sub> grains, localizing at defect sites.

## 1. Introduction

Metal oxides are materials that have received attention as they exhibit a wide variety of electronic behaviour that ranges from good insulators (e.g., Al<sub>2</sub>O<sub>3</sub> and MgO) through wide-bandgap and narrow-bandgap semiconductors (WO<sub>3</sub>, TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>, respectively) to metals (V<sub>2</sub>O<sub>3</sub>, Na<sub>x</sub>WO<sub>3</sub> and ReO<sub>3</sub>) and superconductors (including reduced SrTiO<sub>3</sub>, which is superconducting below 0.3 K, and high-*T<sub>c</sub>* Cu oxides) [1]. Among metal oxides, tungsten trioxide, WO<sub>3</sub>, has proved to be an important material with broad technological applications thanks to its electro-optic, electrochromatic, ferroelectric and semiconducting properties [2–7]. Moreover, recently, it has been used as a sensing material in metal–oxide–semiconductor gas sensors as its electrical properties are greatly influenced by the surrounding atmosphere.

Semiconductor gas sensors based on tungsten trioxide show sensitivity towards traces of pollutant gases such as  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$  and  $\text{NH}_3$  [8–16]. The surface reactivity of  $\text{WO}_3$  towards reducing and oxidizing gases is connected with the presence of oxygen vacancies found in sub-stoichiometric compounds ( $\text{WO}_{3-x}$ ), since in the stoichiometric compound there are no cation d electrons available to be transferred to adsorbates. Three reactions occur independently on the surface of  $\text{WO}_3$  films: (i) gas molecules react with the surface-adsorbed oxygen species and electrons are released; (ii) oxygen species are desorbed by thermal vibrations; and (iii) carrier electrons are trapped by readsorbed oxygen species. Generally speaking the gas detection mechanism is directly related to a change in surface conductivity that appears associated to the release/trapping of electrons during the interaction of gas species with the metal oxide surface [17]. Different contributions to the gas sensing properties of  $\text{WO}_3$  films can be cited: grain size effects in the case of polycrystalline samples, the morphology of the films and the surface chemical concentration, the presence of additives and impurities in the bulk and on the surface. Specifically the addition of transition metal atoms such as Pd, Pt and Ag to  $\text{WO}_3$  films has been shown to considerably influence sensitivity [18–22]. For additive-modified metal oxides, two possible sensing mechanisms have been proposed [23], the distinction between them being related to the origin of the electrochemical changes caused by the gas interaction: an electronic effect (direct exchange of electron between the semiconductors and metal additive particles) and a catalytic one (metallic clusters activate the gaseous species—spillover process).

An important step to gain insight in the sensing mechanism of  $\text{WO}_3$  loaded with noble metals is to understand the modifications induced by metal atoms in the film. It is within this scene that this work was developed, i.e., to analyse the changes induced in  $\text{WO}_3$  films due to Ag loading. This study is motivated by the fact that the addition of Ag to  $\text{WO}_3$  has been shown to improve its sensing properties towards pollutants such as  $\text{SO}_2$  or  $\text{NO}$  [16]. Raman spectroscopy was used to investigate the tungsten oxide lattice and the influence of the addition of Ag on the  $\text{WO}_3$  lattice. X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structure and chemical composition of the films. The morphology of the films was analysed by using atomic force microscopy (AFM).

## 2. Experiment

The  $\text{WO}_3$  films were screen-printed on Si substrates using a printable paste obtained by mixing commercial  $\text{WO}_3$  nano-powders (Sigma-Aldrich) with 1% (in weight) of glass frit. In addition, an organic binder (methyl methacrylate) and an organic solvent (terpineol) were used to achieve good rheology and viscosity, respectively [24]. To produce the  $\text{WO}_3$ :Ag films, the previous paste based on unloaded tungsten oxide was mixed with an Ag paste. Five different levels of silver loading were considered, i.e. pure tungsten oxide and tungsten oxide with 0.5%, 1.0%, 1.5% and 3.0% of Ag in weight. After deposition the films were dried at 150 °C for 2 h, in air. Then two sets of samples were prepared, one fired in air in a belt-furnace at 300 °C and the other at 600 °C.

The materials' composition and changes in their electronic valence band due to Ag loading were analysed by XPS. The x-ray photoelectron (XP) spectra were recorded using an ESCA-300 (SCIENIA, Sweden) photoelectron spectrometer equipped with a monochromatized  $\text{Al K}\alpha = 1486.7$  eV x-ray source. The rotating aluminium anode was operated at 6.4 kW. A high-resolution hemispherical electrostatic analyser with 600 mm diameter and 75 eV pass energy with nominal resolution (source + analyser) 0.4 eV was used [25]. The angle between the incident x-ray and the photoelectron take-off direction was 45°, with the latter normal to the sample surface. The background pressure during experiment was better than  $10^{-9}$  Torr. The binding energy scale was referred to the Ag  $3d_{5/2}$  line at 368.2 eV.

The XPS data processing involved background subtraction and curve fitting. The W 4f core spectrum was analysed using a mixed doublet (Lorentzian–Gaussian) function. The contribution of the W 5p<sub>3/2</sub> peak was taken into account by a mixed singlet (Lorentzian–Gaussian) function. The background due to inelastically scattered electrons was taken into account by a Shirley-type background. The fitting analyses were performed setting a range in which the expected values of the fitting parameters (peak position, peak width, intensity, intensity ratio, mixing ratio and splitting) varied freely. None of them took boundary values.

Raman scattering measurements were carried out to identify the nano-crystallization of the WO<sub>3</sub> films and the evolution of bonds upon Ag loading. The Raman spectra were recorded at room temperature using a Spex 1403 double-pass spectrometer equipped with a RCA31034 cooled photomultiplier tube, using the 514 nm laser line of an Ar laser. The laser power focused onto the sample was 0.25 mW. The resolution of the Raman spectrometer was 5 cm<sup>-1</sup>. The signal of the Si band at 523 cm<sup>-1</sup> originating from the silicon substrate was used for calibration.

Surface morphology and homogeneity of the samples were investigated by AFM (Nanoscope III—Digital Instruments) using a triangular shaped (0.06 N m<sup>-1</sup>) Si<sub>3</sub>N<sub>4</sub> cantilever tip operated in contact mode. The measurements were performed in air.

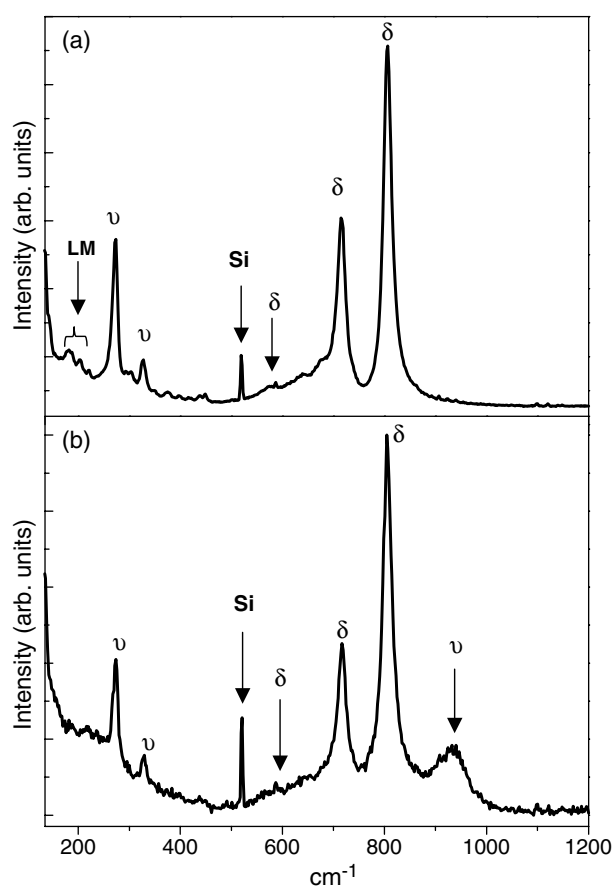
### 3. Results and discussion

Figure 1(a) shows the Raman spectrum recorded on the pure WO<sub>3</sub> film. The presence of stretching vibrational ( $\nu$ ) bands at about 810, 720 and 580 cm<sup>-1</sup>, bending vibrational ( $\delta$ ) bands at about 276 and 330 cm<sup>-1</sup> and of lattice modes near 190 and 138 cm<sup>-1</sup> suggests that the films present the monoclinic phase ( $\gamma$ -WO<sub>3</sub>) [26].

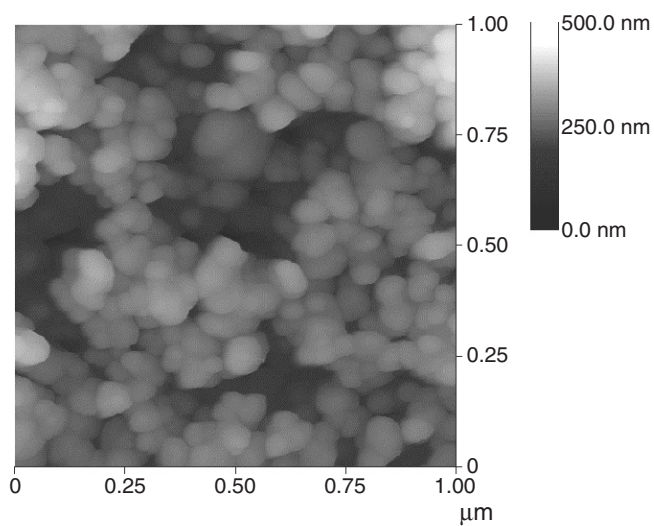
A typical Raman spectrum recorded on the films loaded with Ag atoms is shown in figure 1(b). In addition to the bands observed for pure WO<sub>3</sub> films, films loaded with Ag atoms show a new band peaking at 930 cm<sup>-1</sup> whose intensity increased linearly with increasing Ag content in the sample. This vibrational ( $\nu$ ) band has been reported to be associated with the intercalation of silver atoms into WO<sub>3</sub> tunnels [27, 28].

Figure 2 shows a typical AFM micrograph: the surface of the films was found to be inhomogeneous, and made up of grains and voids. Two factors were found to influence the final grain size: the amount of silver atoms added to the film and the annealing temperature. The grain size was found to increase with increasing annealing temperature. This behaviour was already reported for pure metal oxides [17, 29]. For modified metal oxides, if the firing temperature is high enough to trigger the additive atom diffusion, the increase of the grain size can also be related to the increase of the additive cluster size forming at the surface of the metal oxide grains. In fact an increase in the average grain size from 0.05 to 0.18  $\mu$ m was observed when the amount of silver atom was increased from 0.5% to 3.0% of Ag in weight for a fixed annealing temperature. The annealing allows Ag diffusion in the WO<sub>3</sub> film or on the WO<sub>3</sub> grains. The difference in interface energy between silver clusters and the oxide grains induces the Ag atoms to form clusters at the surface of the oxide grains. Therefore, the increase observed in the average size of grains for increasing levels of Ag loading (at the annealing temperatures studied) can be associated with an increase in the size of Ag clusters and their subsequent coalescence.

An elemental and chemical characterization of the different films was performed by XPS. Figure 3 shows a typical XPS survey spectrum recorded on Ag-loaded samples. It was found that the films are composed of tungsten, oxygen, silver (in the case of Ag-doped films) and traces of adsorbed (<1%) carbon atoms. The low carbon concentration suggests that the organic binder and the solvent used during the film preparation evaporate completely during



**Figure 1.** Raman spectra recorded on (a) a screen-printed tungsten oxide film and (b) a screen-printed tungsten oxide film loaded with 3.0 wt% of Ag.



**Figure 2.** AFM micrographs recorded on a WO<sub>3</sub> + Ag 1.0 wt% sample.

the annealing process. The concentration of silver was found to be 1.8 times larger than the nominal concentration for all the analysed samples annealed at 600 °C. In the case of

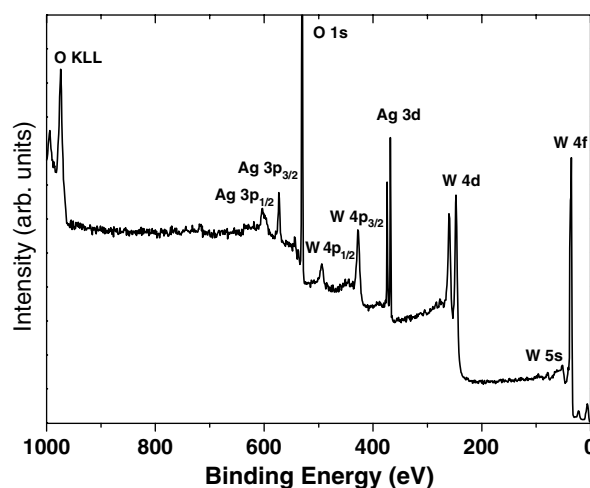
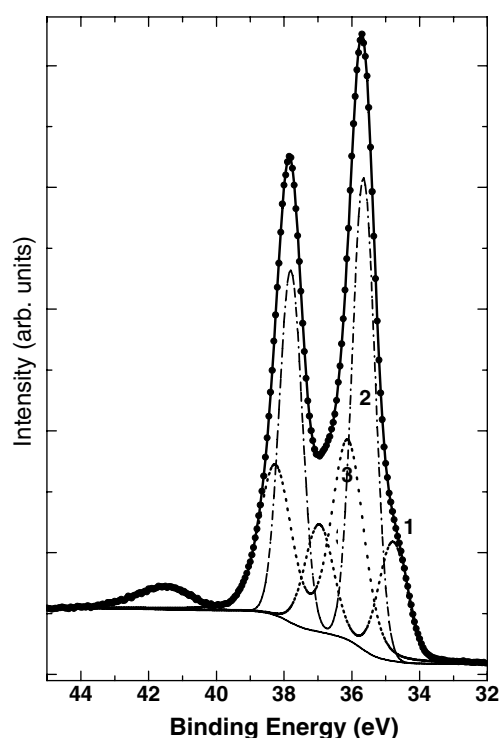


Figure 3. Typical XPS survey spectrum recorded on WO<sub>3</sub> films loaded with Ag.

samples annealed at 300 °C the silver concentration was found to be close to the nominal values. Considering the surface sensibility of the XPS, these results are a strong indication that at high annealing temperature, Ag atoms migrate to the surface of the grains, as suggested by the AFM analysis.

Figure 4 shows the W 4f XP spectrum recorded on a WO<sub>3</sub> sample and its fitting analysis. To reproduce the spectrum, three doublets and the Shirley background were employed. The highest intensity doublet peak (W 4f<sub>7/2</sub>), labelled as 2, located near 35.6 eV, can be associated with photoelectrons emitted from W atoms with oxidation state +6, i.e., stoichiometric WO<sub>3</sub> [9]. In this case the W ions have their 5d shell empty, i.e., there are no cation d electrons available to be transferred to adsorbates. The second W 4f doublet, labelled as 1, found at 1 eV lower binding energy, is generated by photoelectrons emitted from W atoms with oxidation state +5 [30]. In this case, the d-electron orbitals on adjacent cations are partially occupied. These reduced cations provide active sites for chemisorption and catalytic activity, i.e., determine the gas-sensing activity of the films [31]. The third doublet, labelled as 3, at 36.5 eV, has been reported to be associated to surface defects [32], that locally modify the vacuum level  $E_{v1}$  [33]. Therefore, the photoelectrons emitted from the same chemical environment will experience different values of  $E_{v1}$  in traversing the surface, and will arrive at the analyser with a different kinetic energy. In the case of samples with nano-particle morphology, for which the surface area is much extended than for uniform films, the contribution of surface defects can be expected to be quantitatively important in an XPS spectrum recorded using energy of excitation equal to 1486.4 eV.

The W 4f XP spectra recorded on WO<sub>3</sub> samples loaded with Ag were fitted using the same functions as those employed for the pure WO<sub>3</sub> samples. It was found that the contribution to the total W 4f spectrum of the doublet at higher binding energy (36.5 eV) decreased while the Ag loading level increased. The comparison between the spectra recorded on pure WO<sub>3</sub> and on silver loaded film is straightforward if the point-to-point difference between them is plotted, as shown in figure 5. The result of this subtraction indicates that pure WO<sub>3</sub> film has a higher content of oxygen vacancy than the Ag loaded film; the curve of the difference (figure 5) shows a residue associated to the low-energy doublet at 34.6 eV which is generated by photoelectrons emitted from W atoms with reduced oxidation state. Moreover, a signal associated to a rest was also observed for the high-energy doublet at 36.5 eV (figure 5); this is an expected result as the presence of oxygen vacancies is directly connected with surface



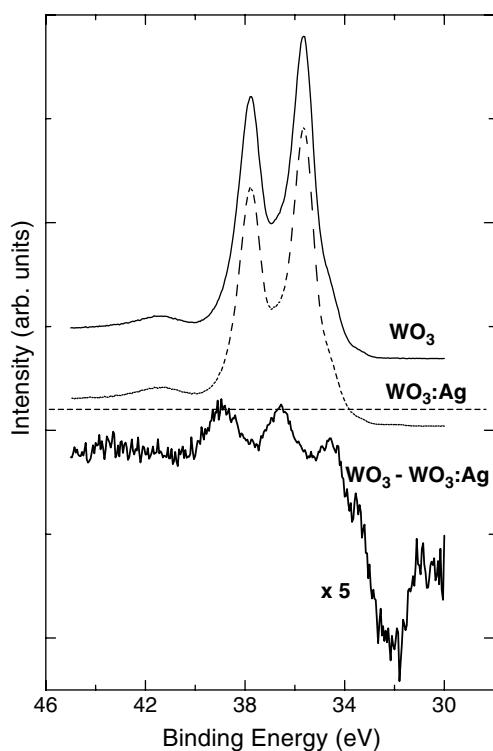
**Figure 4.** W 4f core level spectra recorded on a pure  $\text{WO}_3$  film and the result of its analysis. The doublet peak components are generated by photoelectrons emitted from W atoms with oxidation state +6 (labelled 2) and with oxidation state +5 (labelled 1). The component labelled 3 has been reported to be associated with surface defects [32].

defects. It has been shown that, in some oxides doped with metals, metal atoms diffuse during the annealing process and localize preferentially at defect sites such as oxygen vacancies [1]. If this is the case, Ag atoms migrate to these sites during the annealing procedure and change the electronic density near the W atoms, rendering the surface work function more uniform. This can explain the decrease of both doublet components.

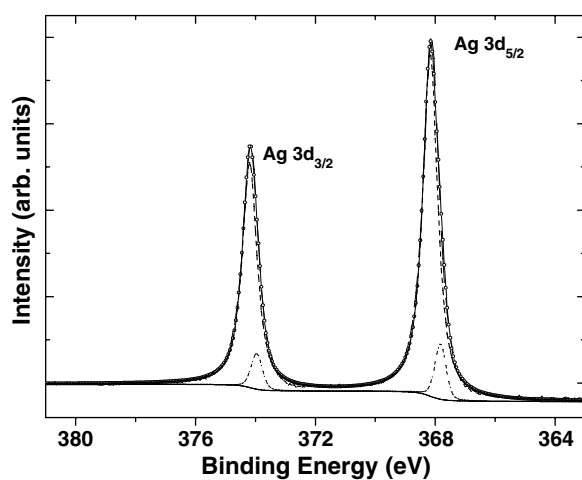
It is important to notice the presence of a structure located at 32 eV in the difference spectrum for which the binding energy is so low that it cannot be associated with photoelectrons emitted from W atoms with oxidation state +4 (figure 5). As suggested by Raman results, Ag atoms migrate in the  $\text{WO}_3$  matrix. From the results discussed before, it can be assumed that the insertion of Ag atoms into the oxide matrix increases the electronic density on the metallic (W) adjacent cation, resulting in higher electronic screening of its nucleus than for the W atom in pure  $\text{WO}_3$  films. As a consequence, the contribution from this cation in the W 4f core level peak is expected to be at a binding energy lower than in the case of pure  $\text{WO}_3$ .

A comment can be raised at this point: if the presence of Ag atoms increases the electron density near W atoms, this makes the W–O bond longer [34, 35]. Thus, in this case one would expect a decrease in the W–O stretching frequency. However, an increase in the W–O stretching frequency was observed in the Raman analysis (see figure 1(b)). To shed light on this discrepancy, it is important to take in account the change in the valence state of W ions, which works in the opposite direction, i.e., decreasing the length of W–O bonds [34, 35]. Therefore, for more ‘reduced’ W states a stronger bonding between tungsten and oxygen ligands is to be expected. It is the interplay of these two antagonistic effects that results in the behaviour observed experimentally.

Figure 6 shows the Ag core level spectrum recorded on the sample loaded with 3.0% of Ag. It is made up of two main components associated with the 3d doublet at 368.2 ( $5d^{5/2}$ )



**Figure 5.** Comparison of the W 4f core level spectra of a WO<sub>3</sub> film (solid curve) and the one associated to WO<sub>3</sub> loaded with 3.0 wt% of Ag (dashed curve).

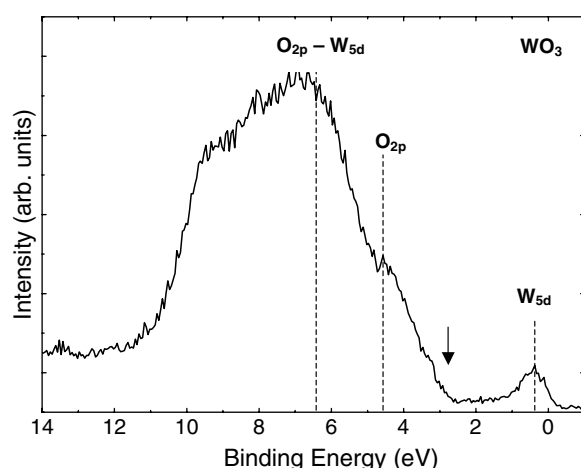


**Figure 6.** Ag 3d core level of WO<sub>3</sub>+3.0 wt% Ag film.

and 374.3 (3d<sup>3/2</sup>). To reproduce this spectrum, two mixed doublets were used: one takes into account the 3d doublet (main components) and the other takes into account the shoulder that appears at the low-energy side of the two main components, at 367.8 eV and at 373.9 eV. These last structures are generated by electrons emitted from Ag atoms in silver oxide [36]. From the Ag spectra recorded on the samples it can be suggested that the Ag clusters are partially oxidized.

In most transition metal oxides, the features appearing in their electronic bands, such as the width of the d bands, are largely a consequence of indirect bonding interactions via metal–



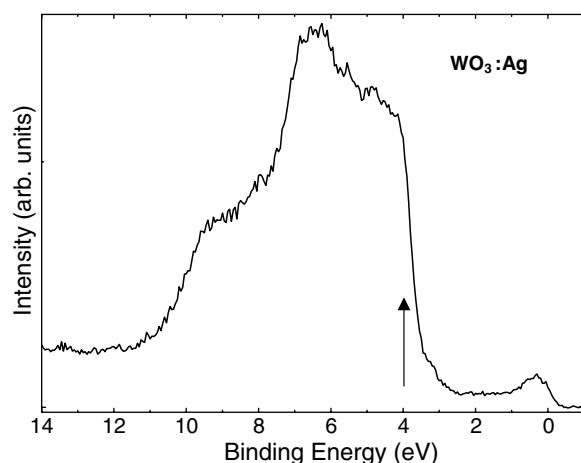


**Figure 7.** Valence spectrum of a pure  $\text{WO}_3$  film.

oxygen–metal linkages, and are thus very sensitive to structural and electronic factors. So the comparison of the recorded valence band with reported data can be used to determine the phase of the metal oxide film that is being studied. The valence band (VB) XP spectrum of the pure  $\text{WO}_3$  film is shown in figure 7. Comparing this VB XP spectrum with literature results, one can associate the spectrum to the one characteristic of a monoclinic phase ( $\gamma\text{-WO}_3$ ) [37, 38]; this supports the suggestion of the Raman results. Covalent bonding interactions transform the O 2p and the metal d orbitals into bonding and antibonding orbitals of mixed atomic character. Calculations of the valence band density of states (VB-DOS) for monoclinic  $\text{WO}_3$  assigned the peak located at about 4.1 eV to an O 2p-derived band while the peak located at about 6 eV corresponds to a hybridized ‘W 5d–O 2p’ band. The rapid onset of the VB spectrum at about 3.0 eV can be assigned to the top of the valence band [37, 38], and the well-defined structure near the Fermi level ( $E_B = 0$ ) is associated to W 5d in-gap states, whose filling is due to the presence of oxygen vacancies [31]. In stoichiometric  $\text{WO}_3$  samples, the 5d-derived states near the gap are empty and no states are observable at the Fermi level [31, 37–39]. However, if there are oxygen vacancies, not all the ‘5d-electrons’ can be transferred and the 5d-derived states near the gap are populated. An alternative interpretation of the VB spectral line shape near the Fermi level based on *ab initio* density functional calculations asserts that, when the concentration of oxygen vacancies is sufficiently high, the Fermi level lies in the conduction band [31, 37–39]. Therefore, the lower binding energy filled states in the VB spectra are conduction band states, which are also derived from W 5d orbitals. Independently of this interpretation, the origin of these states is related to the existence of oxygen vacancies, thus the observation of the near gap structure indicates that the pure  $\text{WO}_3$  film contains oxygen vacancies. Loss of oxygen leaves behind extra electrons and results in pure  $\text{WO}_3$  films behaving as n-type semiconductors. Similar semiconducting properties may be produced by doping with impurities. The insertion of an element into a  $d^0$  oxide may donate electrons and produce an n-type semiconductor; the replacement of an M cation can effectively remove one electron.

The valence band spectra recorded on  $\text{WO}_3$  films loaded with Ag atoms present a new structure peaking at 6.0 eV and, at the same time, the valence band onset shifts to 4 eV (figure 8). Silver has a 4 eV wide s–p band below the Fermi level before the onset of its own 4d bands [40]. Consequently, the shift of the onset can be associated to the Ag s–p band and the new structure to the Ag 4d-like band.

In order to evaluate if there is any hybridization of Ag and  $\text{WO}_3$  valence band states, a numerical procedure was used to simulate the valence band of the  $\text{WO}_3\text{:Ag}$  films by adding



**Figure 8.** Valence spectrum of a WO<sub>3</sub> + 3.0 wt% Ag film.

the valence band spectra of a WO<sub>3</sub> film and of an Ag metal layer. The result of this addition suggests that a simple rigid band model, describing the electronic structure as a superposition of the corresponding reference spectra, is appropriate. This result is contradictory considering the results obtained by analysing the W 4f core levels, which showed the diffusion of Ag atoms in WO<sub>3</sub>. To understand this result we have to consider the morphology of the films which presents Ag clusters and WO<sub>3</sub> grains, so their photoelectron spectra are due to an addition of photoelectrons emitted from WO<sub>3</sub> grains, Ag clusters and from their region of interaction (interface) which is characterized by the intercalation of Ag into WO<sub>3</sub> tunnels, where strong electronic interaction between states is expected [27, 28]. However, due to the very small area (volume) of Ag intercalation, the contribution of photoelectrons generated in this region to the valence spectrum cannot be detected even on the actual high-resolution spectra. Moreover, valence band states present a low cross section for x-ray photo-excitation at the photon energy used.

#### 4. Conclusion

We have observed that the active layers obtained by screen-printing either pure or Ag-loaded WO<sub>3</sub> had a particular morphology made up of voids and grains. Both the Ag loading level and the annealing temperature were found to influence the final grain size. Raman results suggested that, at the interface between tungsten oxide grains and silver clusters, Ag diffuses into the WO<sub>3</sub> matrix.

Oxygen vacancies have been detected by observing: (i) in the W 4f spectra, the presence of a shoulder at 34.6 eV, and (ii) in the VB spectra, the presence of a well-defined W 5d peak near the Fermi level.

To best reproduce the W 4f core level spectrum, three doublets were found to be necessary. They correspond to W atoms with oxidation states +6 and +5 (4f<sub>7/2</sub> localized at 35.6 and 34.6 eV respectively) while the third doublet at 36 eV is associated to surface defects (oxygen vacancies). For increasing levels of Ag loading, the intensity of the doublets at higher (surface defects) and lower (+5 states) binding energy decreased, indicating that during the annealing process, Ag atoms probably migrate to defect sites changing the electronic density near the W atoms by compensating the vacancies. Atomic concentrations obtained by XPS are 1.8 times larger for the samples annealed at 600 °C, suggesting the Ag atoms diffusion onto the WO<sub>3</sub> grains.

The XPS peak at 32 eV binding energy observed in the difference spectrum was associated with photoelectrons emitted from W atoms in the region that Ag atoms diffused into the WO<sub>3</sub>. The Ag spectra recorded on the samples suggest that the Ag clusters are partially oxidized.

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