CHARACTERIZATION AND BUTANOL/ETHANOL SENSING PROPERTIES OF MIXED TUNGSTEN OXIDE AND COPPER TUNGSTATE FILMS OBTAINED BY SPRAY-SOL-GEL

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ABSTRACT

Mixed WO_3 – $CuWO_4$ films have been prepared from aqueous solution of copper sulfate and polytungsten gel with molar ratio Cu/W from 0 to 100 %. These solutions were sprayed onto alumina substrates at 220 ºC. The obtained films were amorphous, and crystallized after an annealing at 300 ºC in air for 3 h. The annealed films were composed by a mixture of $CuWO_4$ and WO_3 phases. The film obtained from a solution with an equimolar ratio of Cu/W was a pure $CuWO_4$. The pure WO_3 films obtained have a high surface "irregularities" (eventually the porosity). Those surface "irregularities" in the films were maintained or eventually increased as Cu/W molar ratio augments in the starting solution up to 10%. The gas sensitivities to butanol and ethanol vapors are also enhanced when the $CuWO_4$ phase increases in the film up to 7% - 10%; further increments to this proportion the detection sensitivity decreases, so compromises are around 7% -10%. The gas sensitivity of pure $CuWO_4$ was lower than pure WO_3.

1. INTRODUCTION

Mixed oxides have been intensively investigated to improve or modify the electrochromic, gas sensing, and photocatalitic properties. For example, the coloration efficiency decreases slightly but the lifetime of WO_3-TiO_2 thin films can be five times longer than of pure WO_3 [1, 2]; mixed oxides have recently emerged as promising candidate for gas detection [3]; and the degradation rate of 1.4-dichlorobenzene was enhanced by addition of WO_3 to TiO_2 [4]. It has been realized that most metal oxides mixtures exhibit increased surface activity.

Simple metal oxides such as SnO_2, WO_3, ZnO and TiO_2 are well known materials that their conductance changes when the composition of the surrounding atmosphere is altered [5]. Different metals and oxides are used as dopants or catalysis in order to be improved the gas sensing properties [6]. It has been concluded that the nature of the surface sites and the electron donor/acceptor properties of the gas, the adsorption, the surface reactions, and the desorption of gases are the key features for the performance of semiconductor gas sensors [5]. Surface properties are expected to be influenced by the grain boundaries between grains of different chemical composition; these phenomena will contribute to the gas sensing properties. Mixed oxides that forms distinct chemical compounds like in the systems Zn-Sn-O [7], Cd-In-O [8], and Sn-W-O [9-12] have been used successfully in gas detection.

Tamaki *et al*. [13] has study different metal tungstates to detect nitrogen oxides, however $CuWO_4$ was missing in that study. A mixture of tungsten oxide and copper oxide heated in vacuum produces $CuWO_4$ with a distorted wolframite type structure [14] and $CuWO_3$ with a cubic structure [15]. The sol-gel technique is well suited for making mixed oxides, and work in W-Ti oxide [1], W-V oxide [16], V-Ti oxide [17], and Fe-Ti oxide [18] has been reported. W_xOP_y films were obtained by spraying the polytungsten gel mixed with H_3PO_4 onto glass substrate at 430 °C showed an improved electrochromism [19]. Combining the spray pyrolysis and the sol-gel techniques has produced very rough films [19]. This technique is very suitable to produce semiconductor metal oxide for gas-sensing applications; due that it yields a large interface between solid and a gaseous medium.

We report in this work the characterization and gas sensing properties of mixed WO_3–$CuWO_4$ films obtained spraying the aqueous solutions of copper sulfate and polytungsten sol onto alumina substrates at 220 ºC. The incorporation of the $CuWO_4$ phase into WO_3 improved the gas response to ethanol and butanol respect to pure WO_3.

2. EXPERIMENTAL

Combined spray pyrolysis and sol-gel techniques were used to obtain mixed tungsten oxide and copper tungstate films on alumina substrates. The process basically consists in producing an aerosol from a gel, which is sprayed on a hot substrate, where the film is going to grow. The outline of the spray system used in this work is described elsewhere [20]. A sol was prepared via acidification of 0.1 M sodium tungstate aqueous solution (pH ~ 7.8) through a proton exchange resin. Different quantities of an aqueous solution of copper sulfate were added to the polytungsten sol to obtain a solution with a molar ratio Cu/W from 0 to 100 % (pH ~ 1 – 1.5). These solutions were sprayed onto alumina substrates at 220 ºC for 45 min.

For gas sensing studies the films were deposited onto alumina substrates with a preprinted gold electrodes, being 0.3 mm apart, and Pt-heating resistor on the reverse side. Rectangular (3 x 2.5 mm^2) mixed WO_3–$CuWO_4$ films were formed so they bridged the gold electrodes. The films were annealed in air by heating at temperatures in the 300 < τ_a < 600 ºC range for 3 h.

3. STRUCTURAL PROPERTIES

The crystal structures of mixed WO_3–$CuWO_4$ films obtained were characterized by x-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). XRD was performed with a Phillips X Pert diffractometer operating with CuK_α radiation, and the infrared spectra were measured in the 450 – 4000 cm^{-1} wave number range using a Shimadzu 8300 spectrophotometer. For FTIR measurements a scratched film from the alumina substrate were mixed with KBr to make a very thin disc.

X-ray diffraction patterns for WO_3 films in as-deposited state and after annealing at 300, 400 and 600 ºC are shown in Fig. 1; the peaks corresponding to the substrate are marked inset with an asterisk. The as-deposited WO_3 film does not show any peak at all. The heat-treated samples crystallize to the monoclinic WO_3 phase. Figure 2 shows the FTIR spectra for as-deposited and annealed (at 300, 400, 500, and 600 ºC) WO_3 films. Both the as-deposited film and that annealed at 300 ºC show a broad band at ~3400 cm^{-1} which is ascribed to O-H stretching mode of water molecules in the films. The broad peak in the region between 600 and 1050 cm^{-1} with a shoulder around 850 cm^{-1} can be attributed to the vibration modes of WO_3 [21]. The broad band of as-deposited WO_3 diminishes as the annealing temperature increases. For gas sensing experiments we used the films annealed at 600 ºC, because the sensing effect is very well known to be optimized at temperatures between 200 and 400 ºC.

Figure 3 shows the X-ray diffractograms for films made from different solutions with Cu/W molar ratio from 0 to 100 % and post-annealed at 600 ºC. Peaks belonging to WO_3 as well as $CuWO_4$ phases are indicated in the figure. The asterisks in the figure represent the peaks due to substrate. Both WO_3 and $CuWO_4$ phases have x-ray diffraction peaks at 2θ in the 22º - 25° range, and the broken lines indicate the Bragg angles of the WO_3 -stronger-peaks in this region. The incorporation of Cu into the WO_3 shows a systematic change of the peaks. Fig. 3 (in set) shows that the films obtained from solutions with a molar ratio Cu/W higher than 3 % present a strong $CuWO_4$ peak at 2θ = 19.05°; therefore, the films obtained from molar ratio Cu/W higher than 3 % have both WO_3 and $CuWO_4$ phases. The amount of the $CuWO_4$ phase in the film increases as the molar ratio Cu/W in the starting solution augments. The film obtained from an equimolar solution of Cu and W was mainly $CuWO_4$.

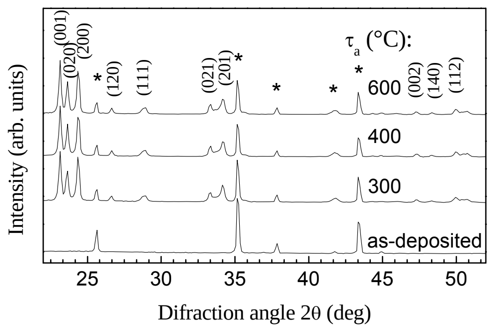

Figure 1. X-ray diffraction patterns for WO_3 films in as-deposited state and after annealed at 300 < τ_a < 600 ºC. Asterisks denote diffraction peaks from the substrate.

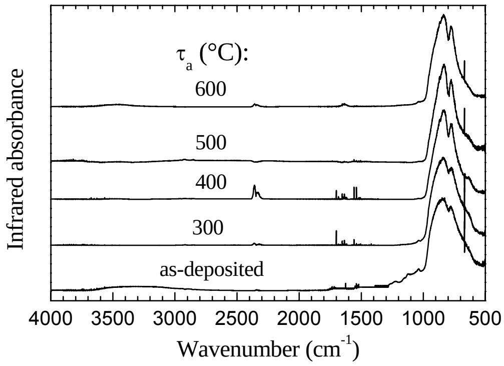

Figure 2. FTIR Spectra measured for WO_3 films in as-deposited state and after annealed at 300 < τ_a < 600 ºC.

The infrared spectra of the films made from solutions with different molar ratio Cu/W from 0 to 100 % and post annealed at 600 °C are shown in Fig. 4. The infrared spectra of the films change as the amount of Cu increases in the spraying solution. The infrared spectrum of pure $CuWO_4$ is in good agreement with those reported by Clark [22] and Arora [23]. The $CuWO_4$ has a strong peak at around 914 cm^{-1} and WO_3 has a broad peak around 850 cm^{-1}; it is hard to detect small concentrations of $CuWO_4$ in the film by infrared spectroscopy. The films prepared from a molar ratio Cu/W higher than 20 % present infrared bands corresponding to both WO_3 and $CuWO_4$ phases. The X-ray diffraction is more sensible to detect small amounts of $CuWO_4$ in the films than infrared spectroscopy, but both results are in agreement in a general context.

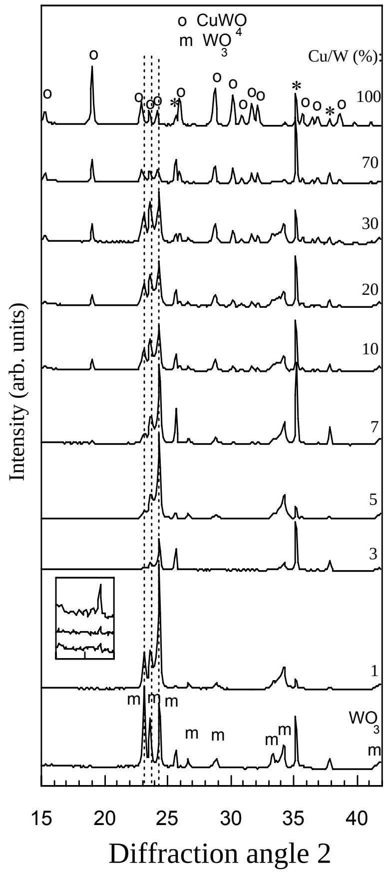

Figure 3. X-ray diffraction patterns for films made from solution with different molar ratio Cu/W after annealing at 600 ºC. Asterisks denote diffraction peaks from the substrate. Diffraction peaks from WO_3 (m) and $CuWO_4$ (o) phases are also indicated. The broken lines indicate the stronger positions of the WO_3. The inset shows the strong peak of $CuWO_4$ at 2θ=19.05º for films obtained from solutions with molar ratio Cu/W 3, 5 and 7%.

The microstructure of the films was analyzed by a scanning electron microscope (SEM), a Hitachi S500 instrument. The morphology of the as-deposited WO_3 films post-annealed at 600°C for 3 h is shown in Figure 5 with low (a) and high (b) magnification. The as-deposited WO_3 film is composed of smooth fibers of around 1.2 μm wide. After annealing the surface of the films became very rough with interconnecting rings: the smooth fibers turn to agglomerated grains. These grains revealed the crystallization of WO_3, which correlate the results from XRD. From micrographs (Fig. 6) one can follow the surface "irregularities" (eventually the porosity) variation of the mixed WO_3-$CuWO_4$ films. The films obtained from solutions of Cu/W molar ratio less than 10 % present surface "irregularities" which start to decrease when films are made from molar ratio of Cu/W higher than 10 %; at this range the density of small spheres starts to increase as Cu/W ratio augments. The morphology of the pure $CuWO_4$ film is composed of agglomerated small grains with a rough surface. A quantitative study of roughness and porosity are going to be performed at further work in order to establish a correlation between Cu/W (%) and roughness (eventually porosity) of the films.

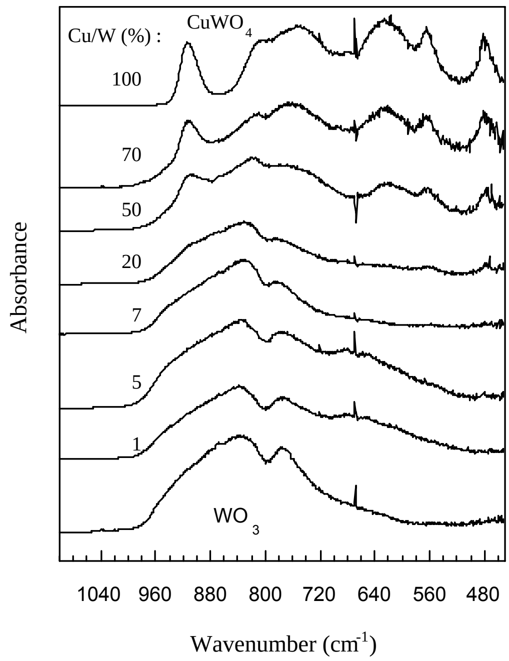

Figure 4. FTIR spectra measured for mixed WO_3–$CuWO_4$ films made from solution with different molar ratio Cu/W after annealing at 600 ºC.

4. GAS SENSING PROPERTIES

Pt-wire contacts were attached with a low-temperature gold paste to the two gold electrodes on the alumina substrate for electrical conductance measurements. The samples under test were placed in a stainless steel chamber (4.4 L) and exposed to different butanol and ethanol vapor concentrations. The films were connected in series with both a known resistor and a 5V source. The conductance of the films was obtained by measuring the voltage drops across the resistor. Gas-sensing properties of the films were studied at various working temperatures τ_o in the $240 < \tau_o < 400$ °C range and using a computer-controlled measuring system.

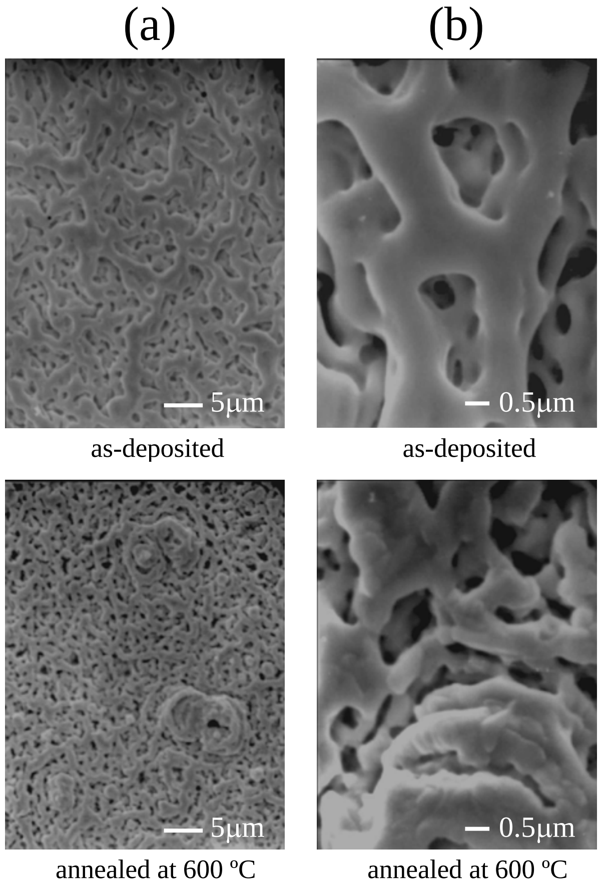

Figure 5. Scanning electron micrographs for WO_3 films as deposited and annealed at 600 ºC in air for 3 h. Parts (a) and (b) refer to low and high magnification, respectively, as apparent from the horizontal bars

The gas sensitivity is defined here as the conductance ratio G_{gas}/G_{air}, where G_{gas} and G_{air} denote the conductance in the test gas and in air, respectively. Figure 7 shows results on the time dependence of conductance, $G(t)/G_{air}$, of a WO_3 film annealed at 600 °C during repeated exposures to 5 ppm of ethanol in air at various working temperatures. The optimum working temperature for WO_3 film to detect ethanol was found to be around 400 °C. Response and recovery times were 10 s and 30 s, respectively. For temperatures lower than 400 °C the conductance variation was small even for long response and recovery times. For this experiment we used a working temperature of 400 °C. The sensitivity of WO_3 film to different concentrations of ethanol and butanol at 400 °C is shown in Figure 8. The sensitivity to butanol has a saturation for concentrations higher than 30 ppm, however the sensitivity to ethanol increases as ethanol concentrations increases according to and approximate power law dependence.

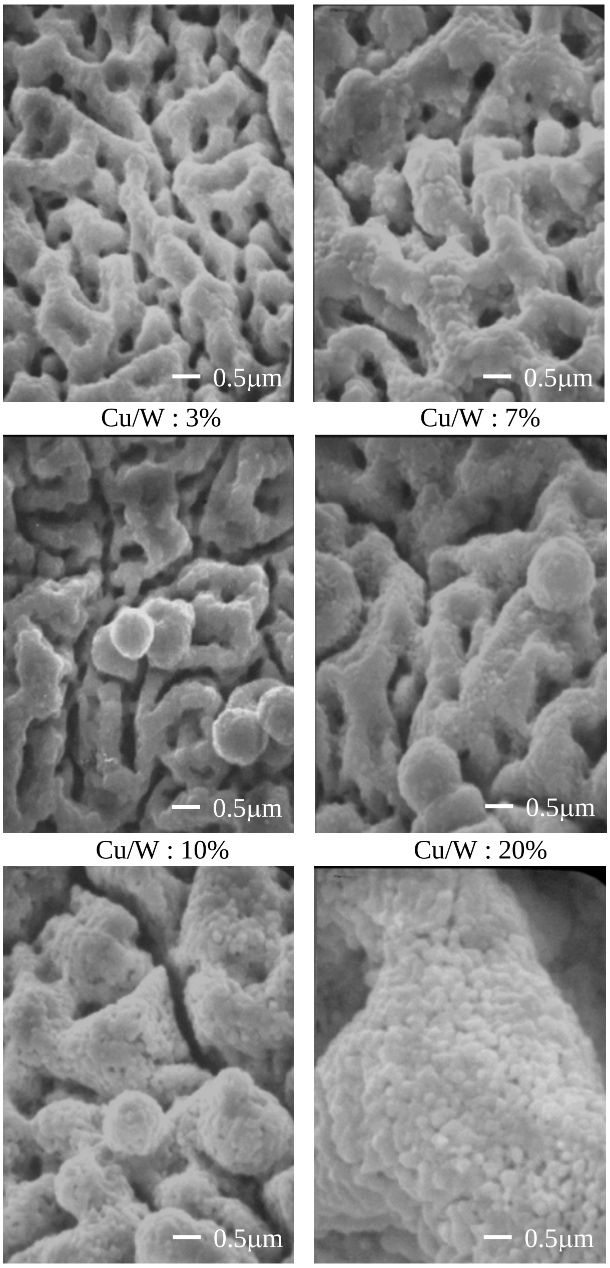

Figure 6. SEM micrographs for mixed WO_3–$CuWO_4$ films after annealing at 600 ºC obtained from solutions with the shown molar ratio Cu/W.

Figure 9 shows results of a detailed study on the gas sensitivity of mixed WO_3-$CuWO_4$ films obtained from different solutions with molar ratio Cu/W from 0 to 100 % after annealed at 600 ºC to 5 ppm of ethanol and butanol. The gas sensitivities to butanol and ethanol vapors are higher for films made from solutions with molar ratio Cu/W lower than 40 % than pure WO_3. The films obtained from solutions with molar ratio Cu/W higher than 40 % have lower gas sensitivity than pure WO_3. It was found the optimal molar ratio Cu/W for the solutions used to prepare the films were 10% and 7% with high gas sensitivity to butanol and ethanol, respectively. The pure $CuWO_4$ film has lower gas sensitivities to ethanol and butanol than WO_3. Response and recovery times for mixed WO_3-$CuWO_4$ films are similar than the pure WO_3.

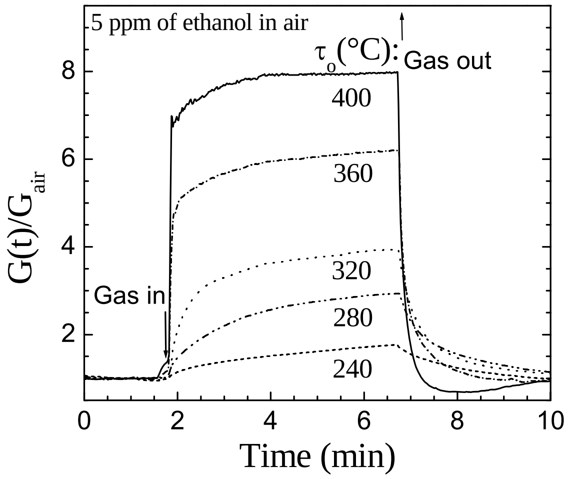

Figure 7. Conductance response vs. time, $G(t)/G_{air}$, of WO_3 film after annealed at 600 ºC, subjected to 5 ppm of ethanol in air at different operating temperatures, τ_o.

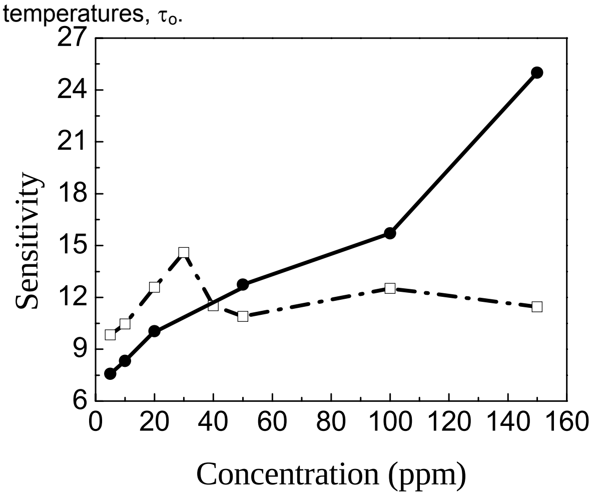

Figure 8. Sensitivity of WO_3 films after annealed at 600 ºC to various concentrations of ethanol (○) and butanol (■) in air. The operating temperature is 400 ºC.

Similar results were reported with 10 wt.% of SnO_2 or ZrO loaded in Fe_2O_3 [24]. The high sensitivity of these sensors were explained on the basis of a SnO_2 or ZrO activity than invokes the acid-based properties of sensing materials towards the sensitive detection ethanol vapor in air [25]. The mechanism of the ethanol sensing is well described by Hellegouar´h et al. [26], and applies to our results.

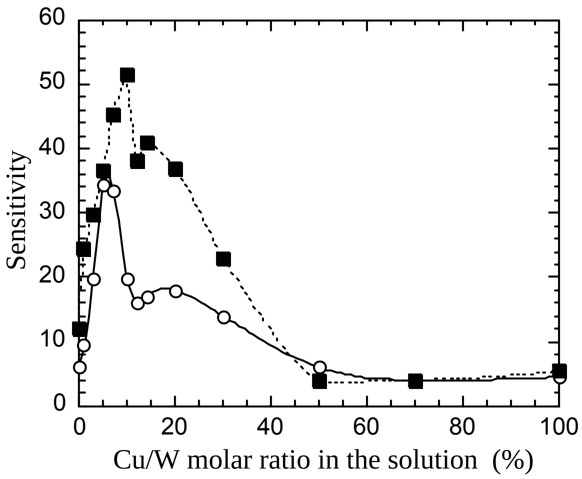

Figure 9. Sensitivity vs molar ratio Cu/W from the solution used to obtain mixed WO_3–$CuWO_4$ films after annealed at 600 ºC, exposed to 5 ppm of ethanol (○) and butanol (■) in air. The operating temperature is 400 ºC.

5. DISCUSSION AND CONCLUSIONS

The annealed films obtained from a solution with molar ratio Cu/W lower than 3 % were mainly monoclinic WO_3, whereas those obtained from solutions with higher Cu/W molar ratios were composed of a mixture of $CuWO_4$ and WO_3 phases. The amount of the $CuWO_4$ phase in the film augmented as the Cu/W molar ratio increased in the starting solution. The film obtained from a solution with a molar ratio Cu/W of 100% was pure $CuWO_4$. The WO_3 films obtained using the combined sol-gel and spray pyrolysis showed high surface ”irregularities” (eventually the porosity). The films obtained from solutions of Cu/W molar ratio up to 10% keep the ”irregularities”, but agglomerate of grains are formed when films are deposited from solutions with higher Cu/W molar ratio than 10%. The morphology of the $CuWO_{4-x}$ films is composed of large crystallites.

The gas sensitivities to butanol and ethanol vapors are enhanced when both WO_3 and $CuWO_4$ phases are present in the films. It was found that optimal Cu/W molar ratio for spraying solutions were around 10% and 7% in order to get high gas sensitivity to butanol and ethanol, respectively. The $CuWO_4$ film has lower gas sensitivities than WO_3.

Therefore the presence of small amounts (less than 10 %) of $CuWO_4$ improves the detection sensitivity of both butanol and ethanol probably due to the change of acid-based properties of the surface in the films [25], but at higher proportions crystallization of $CuWO_4$ predominates diminishing the gas sensitivity detection, so the compromise of both tendencies are about 7-10 %.

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