



Synthesis and evaluation of bis- β -diketonate dioxotungsten(VI) complexes as precursors for the photodeposition of WO_3 films

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ABSTRACT

In this paper non-stoichiometric tungsten oxide thin films have been successfully prepared by direct UV irradiation of bis- β -diketonate dioxotungsten(VI) precursor complexes spin-coated Si(1 0 0) substrates. Photodeposited films were characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) and the surface morphology examined by Atomic Force Microscopy (AFM). The results of XRD analysis showed that the as-photodeposited WO_{3-x} films are amorphous and have a rougher surface than thermally treated films. Post-annealing of the films in air at 500 °C transforms the sub-oxides to a monoclinic WO_3 phase.

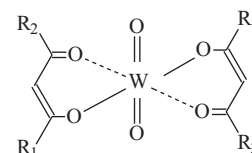
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1. Introduction

Tungsten oxide WO_3 is an n-type semiconductor with interesting physical and chemical properties that make it suitable for various technological applications such as electrochromic devices [1] or gas sensors [2–5]. In particular, WO_3 has remarkable gas sensing properties that account for the considerable attention given for the past few years. As it is known, metal-oxide semiconductor gas sensors are suitable for the detection of oxidizing and reducing gases, since they react to their presence with a measurable change of their electrical conductivity. The mechanism of gas detection with these materials is based, in large part, on reactions that occur at the sensor surface, resulting changes in the electron concentration. Oxidizing gases like NO_2 extract electrons from the conduction band, while reducing ones like NH_3 inject electrons. This change in conductivity is directly related to the amount of a specific gas present in the environment, resulting in a quantitative determination of the gas presence and concentration.

Various deposition techniques for the growth of WO_3 thin films have been reported such as thermal oxidation [6], chemical vapour deposition [7], sol-gel coating [8], e-beam evaporation [9], spray pyrolysis [10], sputtering [11], and laser ablation [12]. In our previous works, we have reported the synthesis of a variety of semiconductor thin films such as NiO [13], MoO_3 [14], ZnO [15], SnO_2 [16], and In_2O_3 [17], using a photochemical method for deposition.

This method, named Photochemical Metal Organic Deposition (PMOD), involves the UV irradiation of films of suitable metal complexes precursors which photodecompose on an appropriate substrate to leave on the surface thin films of metals or metal oxides depending on the reaction conditions. We have found that suitable precursors to be used in this method are β -diketonate metal complexes with alkyl or aryl substituents in the ligand. We therefore proposed β -diketonate dioxotungsten(VI) complexes as precursors for the photochemical deposition of tungsten oxide thin films.



Although numerous dioxomolybdenum(VI) complexes with a variety of supporting ligands have been prepared, the chemistry of analogous tungsten complexes is still inadequately studied [18–20]. One reason for the relatively little number of known dioxotungsten(VI) complexes is the poor availability of suitable starting materials, since typical synthetic routes start from soluble derivatives of WO_2Cl_2 , i.e., $\text{WO}_2\text{Cl}_2(\text{dme})$ [21] and $\text{WO}_2(\text{acac})_2$ [22].

We report here the synthesis of new β -diketonate tungsten-dioxo complexes and a study of their photochemical properties in solution and in solid state. The tungsten(VI)-dioxo complexes have the formula WO_2L_2 , L = acetylacetonate (acac), benzoylacetonate (bac) and 1,1,1-trifluoroacetylacetonate (tfac).

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2. Experimental

2.1. General procedure

The FT-IR spectra were obtained with 2 cm^{-1} resolution in a Perkin-Elmer Model Spectrum One FT-IR spectrophotometer. UV spectra were obtained in a Hewlett-Packard 8452-A diode array spectrophotometer. NMR spectra (400 MHz) were determined with a Bruker Model Avance Digital. Atomic Force Microscopy (AFM) was performed in a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in contact mode. X-ray photoelectron spectra (XPS) were recorded on an XPS-Auger Perkin-Elmer electron spectrometer Model PHI 1257 which included an ultra high vacuum chamber, a hemispherical electron energy analyzer and an X-ray source providing unfiltered $K\alpha$ radiation from its Al anode ($h\nu = 1486.6\text{ eV}$). The pressure of the main spectrometer chamber during data acquisition was maintained at 10^{-7} Pa. The binding energy (BE) scale was calibrated by using the peak of adventitious carbon, setting it to 284.8 eV. The accuracy of the BE scale was $\pm 0.1\text{ eV}$. High resolution spectra were always fitted using Gaussian-Lorentzian curves in order to more accurately determine the BE of the different element core levels. Prior to curve fitting, a background was subtracted by the method devised by Shirley [23]. The approximate composition of the surface was determined by dividing the individual peak area, after appropriate background subtraction, by their respective atomic sensitivity factor (ASF). X-ray diffraction patterns were obtained using a Bruker D8 Advance diffractometer. The X-ray source was Cu 40 kV/40 mA. Film thickness was determined using a Leica DMLB optical microscope with a Michelson interference attachment.

2.2. Materials

WO_2Cl_2 , WCl_6 , $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$, acetylacetone (acacH), 1-benzoylacetone (Hbac), 1,1,1-trifluoro-2,4-pentanedione (tfacH), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) were all obtained from Aldrich Chemicals and used without further purification. All solvents were distilled and dried by standard methods before use. Other diketones such as 1-phenyl-1,3-nonanedione, and 2,8-dimethyl-4,6-nonanedione were synthesized by a modified procedure by Adams and Hauser [24].

2.3. Syntheses of β -diketonate dioxotungsten(VI) complexes

$\text{WO}_2(\text{acac})_2$ was prepared by a modification of the method of Nikolovski [25]. A solution of 0.011 mol (3.05 g) of WO_2Cl_2 and 0.195 mol (20 mL) of acetylacetone in 50.0 mL of dry toluene was refluxed for 12 h. The volume was reduced to one-half and the solution stored in the freezer for 24 h. A small amount of anhydrous diethyl ether was added and the pale yellow precipitate collected, washed with four 10.0-mL portions of diethyl ether, and dried over MgSO_4 . Yield: 1.77 g (38.8%); m.p. $201.3\text{ }^\circ\text{C}$; IR (KBr, cm^{-1}): 1588 (vs C=O), 1518 (vs C=C), 955 (vs W=O), 909 (vs W=O); UV-Vis (in EtOH) λ_{max} (log ϵ): 274 (3.94). *Anal. Calc.* for $\text{C}_{10}\text{H}_{14}\text{O}_6\text{W}$: C, 29.01; H, 3.41. Found: C, 29.12; H, 3.38%.

Other diketonate dioxotungsten(VI) complexes were prepared using $\text{WO}_2(\text{acac})_2$ as the starting material by the following general procedure: The corresponding diketone ligand (2.00 mmol) was added to a solution of $\text{WO}_2(\text{acac})_2$ (1.00 mmol) in 25 mL of dried methanol. After refluxing for 45 h the reaction mixture was filtered, and the filtrate was evaporated under reduced pressure to dryness. To the residual solid, pet-ether was added and the solid separated by vacuum filtration to give the corresponding complexes.

$\text{WO}_2(\text{bac})_2$: yield 36%; m.p. $219\text{--}221\text{ }^\circ\text{C}$; IR (KBr, cm^{-1}): 1592 (vs), 1555 (vs 1489 (vs C=O, C=C); 962 (s, W=O), 875 (vs W=O);

^1H NMR (400 MHz, CDCl_3 , δ ppm): 2.21 (s, 3H), 6.19 (s, 1H), 7.44 (t, 2H), 7.53 (t, 1H), 7.88 (2H); ^{13}C NMR (100.6 MHz, CDCl_3 , ppm): 25.84, 96.68, 126.98, 128.59, 132.26, 134.86, 183.32, 193.77; UV-Vis (in EtOH) λ_{max} (log ϵ): 249 (3.87), 310 (4.30). *Anal. Calc.* for $\text{C}_{20}\text{H}_{18}\text{O}_6\text{W}$: C, 44.63; H, 3.37. Found: C, 44.71; H, 3.29%.

$\text{WO}_2(\text{tfac})_2$: yield 13%; m.p. $168.5\text{--}169.7\text{ }^\circ\text{C}$; IR (KBr, cm^{-1}): 1627 (vs C=O), 1570 (sh, C=C), 980 (vs W=O), 901 (vs W=O); UV-Vis (in EtOH) λ_{max} (log ϵ): 279 (3.63). *Anal. Calc.* for $\text{C}_{10}\text{H}_8\text{F}_6\text{O}_6\text{W}$: C, 23.01; H, 1.54. Found: C, 23.29; H, 1.72%.

$\text{WO}_2(\text{hfac})_2$: yield 23%; m.p. $134.6\text{--}135.8\text{ }^\circ\text{C}$; IR (KBr, cm^{-1}): 1639 (vs C=O), 1582 (C=C), 969 (vs W=O), 897 (vs W=O); UV-Vis (in EtOH) λ_{max} (log ϵ): 281 (3.46). *Anal. Calc.* for $\text{C}_{10}\text{H}_2\text{F}_{12}\text{O}_6\text{W}$: C, 19.07; H, 0.32. Found: C, 19.25; H, 0.29%.

2.4. Photolysis of complexes in solution

Solution photochemistry was carried out in 1 cm quartz cells, which were placed in a Rayonet RPR-100 photoreactor equipped with 254 nm lamps. Progress of the reactions was monitored by determining the UV spectra at different time intervals, following the decrease in UV absorption of the complexes.

2.5. Preparation of amorphous thin films

The substrates for deposition of films were borosilicate glass microslides ($2 \times 2\text{ cm}$, 1.1 mm thickness, Specialty Glass Products, Penn.) and p-type silicon(1 0 0) wafers ($1 \times 1\text{ cm}$) obtained from WaferNet, San Diego, CA, or University Wafer, Boston, Massachusetts. Prior to use the wafers were cleaned successively with ether, methylene chloride, ethanol, aqueous HF (50:1) for 30 s and finally with deionized water. They were dried in an oven at $110\text{ }^\circ\text{C}$ and stored in glass containers.

The thin films of the precursor complexes were prepared by the following procedure: A portion (0.5 ml) of a solution of the diketonate complex in CH_2Cl_2 was dispensed onto a silicon chip placed on a spin coater and then rotated at a speed of 1500 rpm and allowed to spread. The motor was then stopped and a thin film of the complex remained on the chip. The quality of the films was examined by optical microscopy.

2.6. Photolysis of complexes as films on Si surfaces

The solid state photolysis was carried out at room temperature under a UVS-38 254 nm lamp equipped with two 8 W tubes, in an air atmosphere.

All photolysis experiments were done following the same procedure. A typical experiment is described. A film of the diketonate complex was deposited on p-type Si(1 0 0) by spin-coating from a CHCl_3 solution. This resulted in the formation of a smooth, uniform coating on the chip. The FT-IR spectrum of the starting film was first obtained. The chip was then placed under a UVS 254 nm lamp. After the IR spectrum showed no evidence of the starting material, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface, prior to analysis.

3. Results and discussion

In recent years, we have developed a photochemical method for the deposition of a variety of metals and oxides [13–17]. In this method, thin films of inorganic or organometallic precursors upon irradiation are converted to amorphous films of metals or metal oxides, depending on the reaction conditions. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin coating onto a suitable substrate,

and that photolysis of these films results in the photoextrusion of the ligands leaving the inorganic products on the surface.

In this work several diketonate dioxo complexes of W(VI) of the type $\text{WO}_2(\text{R}^1\text{COCHCOR}^2)_2$ were investigated in order to determine if they formed good amorphous films upon spin coating. Although it was found that most of the above complexes form good quality films, the best results were observed with the complexes where $\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{methyl}$, and $\text{R}^1 = \text{CF}_3$, $\text{R}^2 = \text{methyl}$. These compounds can be spin coated from chloroform solutions onto a suitable substrate such as borosilicate glass or a Si(100) chip, forming amorphous films showing no sign of crystallization on examination under an optical microscope up to $1000\times$ magnification. These complexes also showed the highest photosensitivity in solution as well as a film, of all the β -diketonate derivatives. For further study we hence concentrated on WO_2L_2 complexes with 1,3-butanedione and 1-phenyl-1,3-pentanedione as ligands.

3.1. Synthesis of complexes

As mentioned above, one of the reasons for the little number of known dioxotungsten(VI) complexes is the poor availability of suitable starting materials. In some cases, tungstate ion $[\text{WO}_4]^{2-}$ can be used in acidic, aqueous solution to prepare new *cis*-dioxotungsten(VI) complexes [13,26]. Other procedures employ moisture-sensitive, poorly soluble $[\text{WO}_2\text{Cl}_2]$ or its more convenient derivatives, i.e. $[\text{WO}_2\text{Cl}_2(\text{dme})]$ and $[\text{WO}_2(\text{acac})_2]$ (dme = 1,2-dimethoxyethane) [18b,22,27]. Literature known synthetic routes starting from the commonly used WO_2Cl_2 usually include adducts or ligand exchange reactions. In this work we performed the direct synthesis of a dioxotungsten(VI) complex with two diketonate ligands using WO_2Cl_2 as starting material. These attempts did not afford very good yields of the complexes mainly because of the low solubility and instability of the starting material. The best results were obtained when acetylacetonone was used as ligand and the yields of $\text{WO}_2(\text{acac})_2$ were close to 40%. The literature method to obtain $\text{WO}_2(\text{acac})_2$ from WO_2Cl_2 was improved by using toluene instead of benzene as solvent and filtering right out of the reaction flask with a drain tube while still refluxing. Thus, the yield reported by Yu and Holm was increased from 44% to 77% and the reaction time was reduced from 48 to 9 h [28,22]. Since acetylacetonate complexes have proven to be useful in ligand exchange reactions, we chose $\text{WO}_2(\text{acac})_2$ as a suitable precursor for further complex synthesis with other diketonate ligands.

We obtained dioxotungsten(VI) complexes of the type WO_2L_2 with diketonate ligands by ligand exchange with two equivalents of the diketone in methanol. Depending on the ligand, the products precipitate after reducing the volume of the solvent and yields between 10% and 40% were achieved.

The characterization of the complexes was carried out by infrared spectroscopy and, when possible, by NMR. The infrared spectra of two complexes, $\text{WO}_2(\text{acac})_2$ and $\text{WO}_2(\text{bac})_2$ are shown in Figs. 1 and 2, and the frequencies of the observed bands for each complex are listed in the Section 2. As can be seen from the figures the spectra of the chelates with Hacac and Hbac were similar, except of course for the bands attributable to vibrations located mainly in the phenyl rings. For the assignment of the ligand bands in the $1600\text{--}1500\text{ cm}^{-1}$ region it has been established by Behnke and Nakamoto [28] that the higher-frequency band belongs to a predominantly C=O vibration and the lower frequency-one to a predominantly C=C vibration. The assignment of all other bands found in this region and attributable to vibrations located mainly in the ligand rings seems to be rather well-established and, therefore, straightforward.

Apart from the ligand bands, in the spectrum of the $\text{WO}_2(\text{diketonate})_2$ complexes one can find two intense absorption peaks at ca. 900 and 950 cm^{-1} which are undoubtedly due to the symmetric

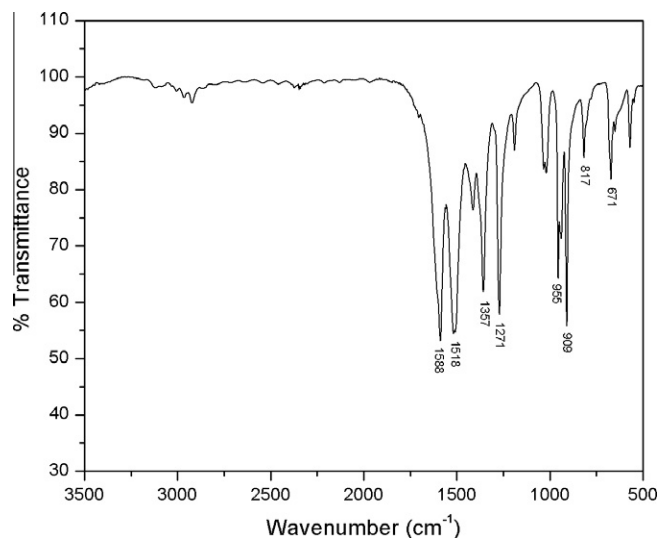


Fig. 1. Infrared spectrum of the complex $\text{WO}_2(\text{acac})_2$ (KBr pellet).

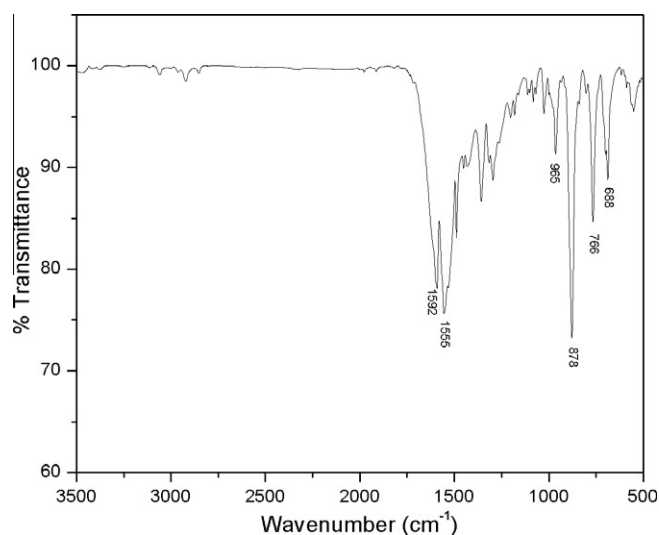


Fig. 2. Infrared spectrum of the complex $\text{WO}_2(\text{bac})_2$ (KBr pellet).

and asymmetric stretching vibrations of the WO_2^{+2} group. The existence of two W=O stretching bands strongly suggests that the WO_2^{+2} group in the dioxotungsten diketonate complexes is not linear and reflects the asymmetric *cis*-dioxo structure, which has been described in the literature for other dioxotungsten complexes.

Because of the higher solubility of the $\text{WO}_2(\text{bac})_2$ complex this compound could also be characterized by ^1H and ^{13}C NMR (the data is shown in the Section 2).

3.2. Solution photochemistry

Although the photochemistry of several transition metal 1,3-diketones has been extensively studied [29], no reports can be found in the literature concerning tungsten diketonate complexes. We therefore carried out experiments to evaluate the photosensitivity of the complexes $\text{WO}_2(\text{acac})_2$ and $\text{WO}_2(\text{bac})_2$. When ethanol solutions of these complexes were photolyzed with 254 nm UV light, a rapid decrease in the absorption bands of the $\text{WO}_2(\text{acac})_2$ and $\text{WO}_2(\text{bac})_2$ complexes could be observed after 120 and 40 min of irradiation, respectively. Fig. 3 shows the UV profile of

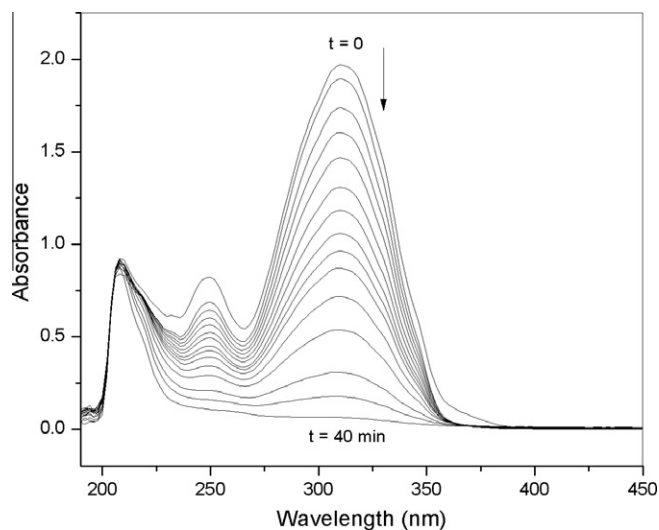


Fig. 3. Changes in the UV spectrum of a solution of $\text{WO}_2(\text{bac})_2$, dioxobis(1-phenyl-1,3-butanedionato)tungsten(VI) (3.41×10^{-5} M in EtOH) upon 40 min irradiation with 254 nm light (4 min intervals).

the photoreaction obtained by determining the UV spectra of samples taken at 4 min intervals for $\text{WO}_2(\text{bac})_2$. These results demonstrated that both diketonate dioxotungsten(VI) complexes are highly photoreactive in solution when irradiated with 254 nm UV light. Irradiation of $\text{WO}_2(\text{bac})_2$ at the low-energy band with 300 nm light did not cause any change in the UV spectrum.

3.3. Solid state photochemistry

Thin films of $\text{WO}_2(\text{acac})_2$ and $\text{WO}_2(\text{bac})_2$ were prepared by spin-coating ethanol solutions of the complexes on Si(1 0 0) chips. The FT-IR spectra were similar to those obtained for crystalline samples.

Irradiation of thin films (~ 400 nm thickness) of $\text{WO}_2(\text{acac})_2$ and $\text{WO}_2(\text{bac})_2$ under air atmosphere, led to the disappearance of the absorptions associated with the ligand, as shown by the FT-IR monitoring of the reaction (Fig. 4). At the end of the photolysis there are no detectable absorptions in the infrared spectrum. These

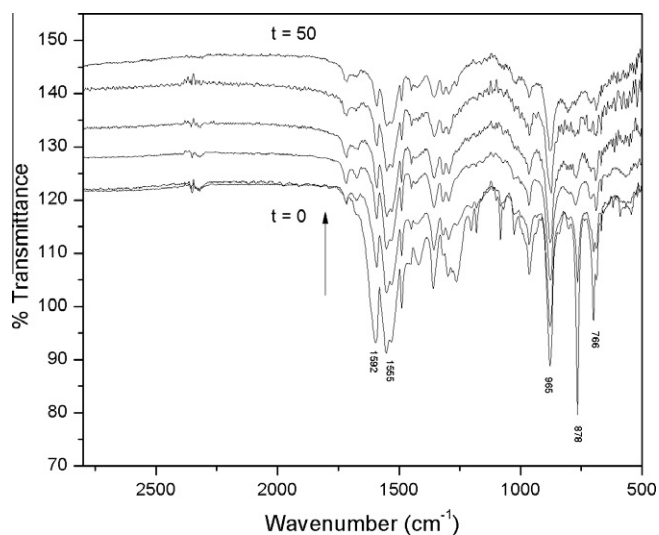


Fig. 4. Changes in the FT-IR spectrum of a film of $\text{WO}_2(\text{bac})_2$, bisdioxo(1-phenyl-1,3-butanedionato)tungsten(VI) (400 nm thickness) upon 50 min irradiation with 254 nm light.

results suggest that the diketonate groups on the precursors are photodissociated on the surface forming volatile products which are readily desorbed from the surface.

FT-IR spectroscopy was also used to characterize the photodeposited films. Fig. 5 shows the FT-IR spectrum of a 400 nm film deposited on a polished Si wafer from a $\text{WO}_2(\text{bac})_2$ precursor. As-deposited films show a single broad absorption between 550 and 900 cm^{-1} . This band is attributed to the stretching vibration of W–O bonds, and is usually observed at around 730 cm^{-1} [30]. After annealing for 3 h at 500 °C, the spectrum exhibits W–O–W framework absorption over the same spectral region but with a more resolved peak occurring between 720 and 800 cm^{-1} . These WO_3 absorption properties are similar to those observed in thicker films [31].

XRD characterization of the as-deposited films reveals the amorphous nature of these films since no diffraction peaks could be observed (Fig. 6a). However, XRD spectra for films annealed at 500 °C show a well-developed crystalline structure (Fig. 6b), with reflections that could be assigned to crystalline monoclinic WO_3 structure. The spectrum of the annealed films showed XRD lines

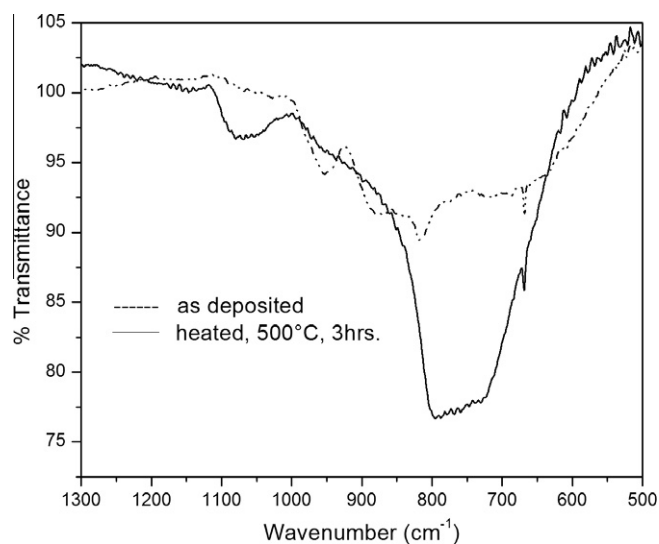


Fig. 5. FT-IR spectrum of a film of WO_3 (400 nm thickness) on a Si(1 0 0) wafer, as-deposited and annealed at 500 °C for 3 h.

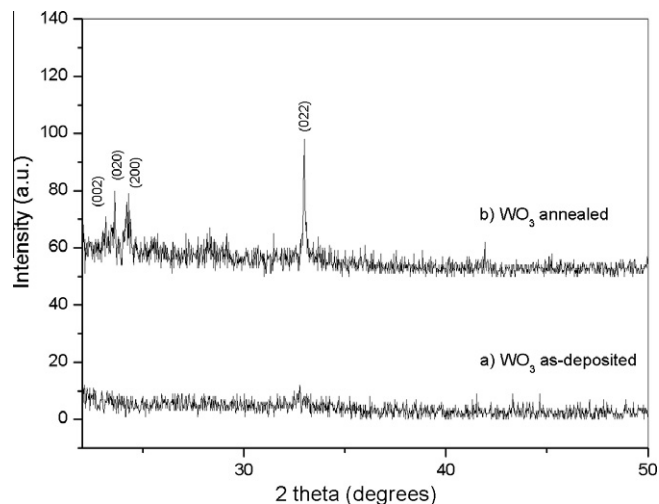


Fig. 6. XRD pattern of a photodeposited WO_3 film (250 nm thickness): (a) as-deposited and (b) annealed in air at 500 °C for 4 h.

at $2\theta = 23.1^\circ$, 23.6° , 24.3° , and 33.1° corresponding to the (0 0 2), (0 2 0), (2 0 0) and (0 2 2) planes of the monoclinic WO_3 phase (JCPDS 72-1465). This indicates that films exhibit a strong (0 2 2) preferred orientation.

In order to determine the film surface composition we carried out an XPS analysis. Fig. 7 shows the wide scan XPS spectrum, in the binding energy range of 0–1000 eV, of an annealed WO_3 film photodeposited on a Si(1 0 0) surface. The spectrum shows that the main constituent elements of annealed films were tungsten and oxygen atoms, except for additional minor peaks resulting from carbon and Si. The appearance of Si 2s and 2p signals can be attributed to photoelectrons ejected from the Si substrate due to the highly porous nature of the films. Although it has been argued that the presence of phenyl rings in the precursors often introduces carbon impurities in MOCVD of other metals [32], the carbon detected on the surface of the photodeposited film is probably the result of contamination rather than an inefficient photolysis. After 60 s Ar^+ sputtering no carbon was detected on the film surface.

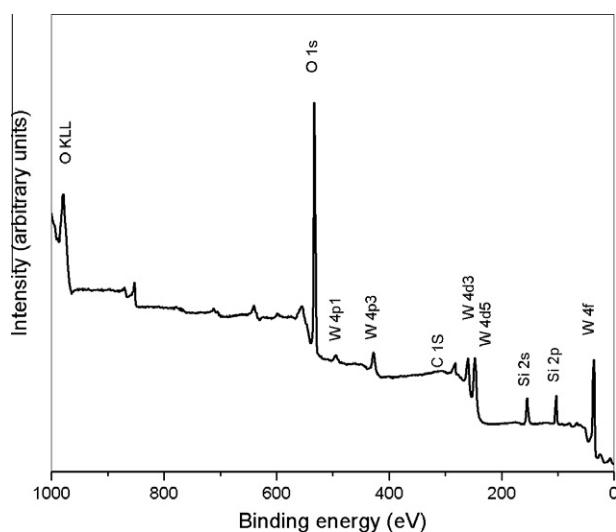


Fig. 7. Wide-scan XPS spectrum of a photodeposited WO_3 film annealed under air atmosphere at 500°C for 3 h.

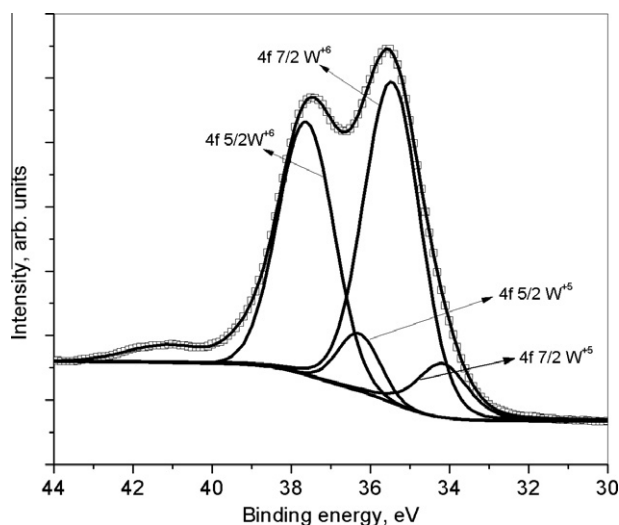


Fig. 8. Narrow scan W 4f XPS spectrum of photodeposited WO_3 films annealed under air atmosphere at 500°C for 3 h.

High resolution spectra of W 4f and O 1s photoelectron lines for annealed WO_3 thin film surface were recorded (Figs. 8 and 9, respectively).

The W 4f core level spectrum recorded on samples annealed at 500°C shows two groups of W 4f doublets after peak fitting (Fig. 8). The two components associated with W $4f_{5/2}$ and W $4f_{7/2}$ spin orbit doublet at 37.6 and 35.4 eV, respectively. These values are in agreement with those found in the literature for W^{+6} in WO_3 stoichiometric films [33]. The other doublet with BE values of 34.13 and 36.24 eV for W $4f_{7/2}$ and W $4f_{5/2}$ respectively, corresponded to a W^{+5} state according to values reported in the literature [34–36]. The formation of these reduced states could be due to over irradiation of the WO_3 films during the photodeposition process. It has been reported that W^{+5} species are formed when WO_3 films are irradiated with UV light [37].

It can be seen in the spectrum shown in Fig. 9, that the O 1s peak consists of two contributions separated by approximately 2.35 eV. The first component located at a lower energy

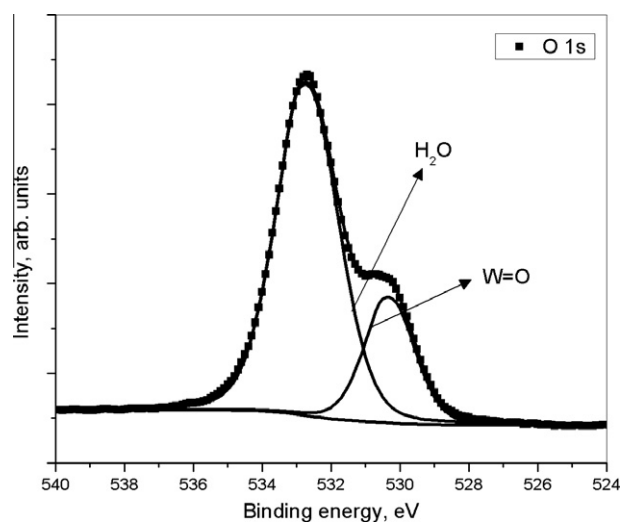


Fig. 9. Narrow scan O 1s XPS spectrum of an annealed WO_3 film and the peak-fitted signals.

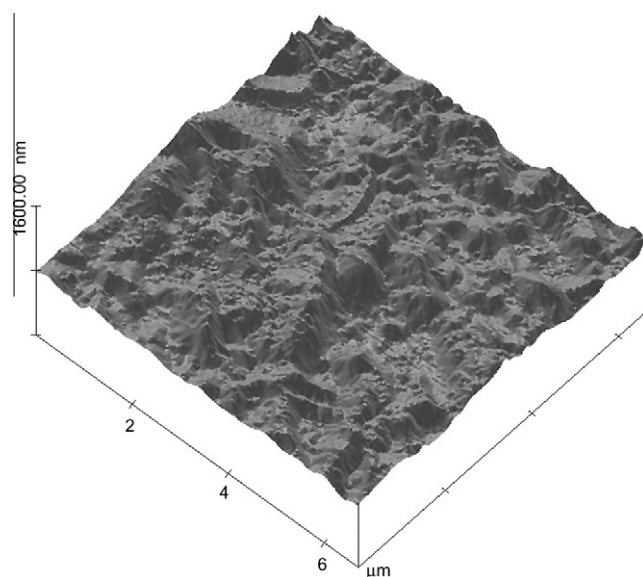


Fig. 10. AFM micrograph of an as-deposited WO_3 thin film on Si(1 0 0). Image size $7 \times 7 \mu\text{m}$, with z-scale of 1600.0 nm.

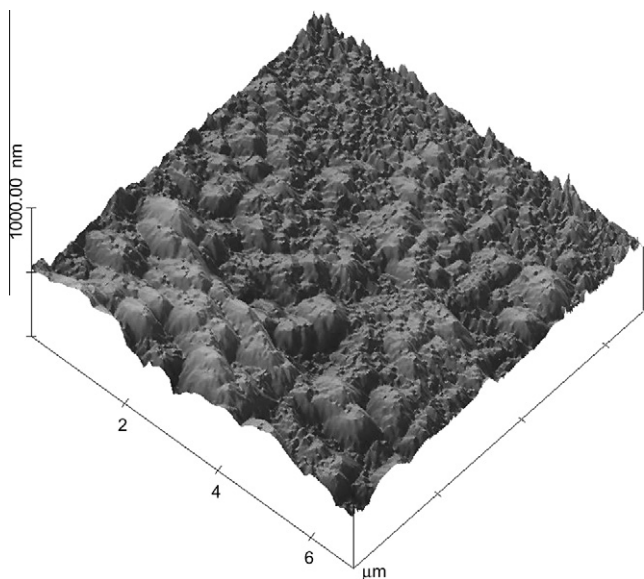


Fig. 11. AFM micrograph of an annealed (500 °C, 3 h) WO_3 thin film deposited on Si(1 0 0). Image size $7 \times 7 \mu\text{m}$, with z-scale of 1000 nm.

(530.31 eV) is assigned to the oxygen atoms that form the strong $\text{W}=\text{O}$ bonds in the oxide [38]. The second O 1s peak, located at a higher energy (532.66 eV), corresponds to oxygen in water molecules bound in the film structure or adsorbed on the sample surface [39,40].

The amorphous characteristic of the as-deposited WO_3 films was also by the morphological analysis of the film surface. Figs. 10 and 11 showed three-dimensional AFM images of as-deposited (Fig. 10) and annealed (Fig. 11) WO_3 films.

The as-deposited film showed a non-uniform rough surface with a root-mean-square (rms) roughness of 56.7 nm and a maximum height, R_{max} , of 356 nm (Fig. 10). This surface can be described as fibrous-type without a structural order, which is characteristic of an amorphous deposit. On the other hand, the annealed WO_3 film showed a more uniform and smoother surface with a rms roughness of 36.1 nm and a R_{max} of 325 nm (Fig. 11). It can be observed the formation of a crystalline film with small grains ranging in size from 1 to 3 nm.

4. Conclusions

WO_3 thin films have been successfully prepared by direct UV irradiation of amorphous films of bis-dioxo(1-phenyl-1,3-butanedionato)tungsten(VI) complexes on Si(1 0 0) substrates. X-ray photoelectron spectroscopy (XPS) results showed that the resulting films are non-stoichiometric. The surface characterization of these thin films was performed using Atomic Force Microscopy (AFM), revealing that as-deposited tungsten trioxide films have a rougher surface than thermally treated films. In this direct photodeposition method, the amorphous characteristics of the precursor complexes strongly determine the non-crystalline nature of the as-deposited metal oxide films.

Acknowledgments

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