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CVD - technology of transition metal oxides and their impact on solar energy utilization

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Abstract. The paper presents results concerning CVD thin films of transition metals (W and Mo) and their composite structures $\text{WO}_2:\text{W}$ and $\text{MoO}_2:\text{Mo}$, as well as WO_3 films. The composite structure materials consisting of a suspension of metallic molybdenum or tungsten grains in a host matrix of metal dioxide demonstrate significant solar absorptance coupled with a high infrared reflectance, which is necessary for efficient conversion of solar energy into heat. Transition metal trioxides thin films, known as electrochromic materials have been studied with respect to the technological conditions for their growth. It is found that they start to grow up at temperatures in the range of 500 °C. Spectral transmittance and the structure of WO_3 films were investigated.

1. Introduction

The remarkable growth of solar energy technology over the last decade has created a demand for novel optical coatings. The total efficiency of solar energy system will critically depend on its reflecting, absorbing and transmitting components. The collective surface must be spectrally selective. With other words, it must combine high solar absorptance a_s and low thermal emittance e_t . In order to be cost effective the coating must have long life-time at the operating temperature. Economic, large scale production is important as large areas of solar flux must be intercepted. It follows, that simplicity of design would be an especially attractive property for conversion surface [1,2]. During last decade, starting from the Optical Science Center at the University of Arizona, we have been

intensively studying black molybdenum and black tungsten thin films spectrally selective surfaces. They are one layer structures, easy to be made, merely by proper choosing of precursors (source materials) and by proper technological steps [3]. We have used Chemical Vapor Deposition of oxichlorides as well as hexacarbonyls. We found that oxygen presence in the chemical reaction makes it possible for black metals spectrally selective surfaces to be made. Optimization of the technological parameters of the processes applied to generate the above mentioned materials as well as studying of their phase structure in order to find the temperature range where WO_3 starts to grow up was the purpose of the present work. This thin film material is interesting as a chromogenic material. Since the time when the paper of Deb [4] appeared, the chromogenic materials have been under attention of many researchers. WO_3 is one of the most promising electrochromic material. The electrochromic materials are able to change their optical transmittance when a small voltage is applied. This change is reversible and the effect may last for long time [5-7]. Of course, the phenomenon is not in a single layer, but the electrochromic layer is the active part of a device. WO_3 is a very interesting with respect to the so called "smart windows" application - buildings and automobiles windows may be smart to change their colours in a way to save energy (electrical one for lighting) or to make driving comfortable having rear-view mirrors with anti-dazzling effect. Many other applications are also possible .

2. Deposition and Measuring Technics

All results presented are made on samples obtained and annealed in a CVD-system, built up as follows: The sublimator is immersed in a silicon oil bath, the temperature of which is controlled with an accuracy of $\pm 1^\circ\text{C}$. The lines in the CVD-equipment are PFA-Galtek type teflon tubes and fittings are wrapped by heating tapes to keep the temperature of the lines equal to the one of sublimator or higher. Substrates, being stainless steel for black metal coatings, or glass ones (either quartz or "Float"-type glass) for WO_3 films are situated on a graphite susceptor, heated by a high frequency generator. The substrate temperature is controlled by switching off one of the three phases of generator using a thermoregulator. Special cares were taken for the Pt-Pt/Rd thermocouple to be isolated from the electromagnetic field. The gases used were argon (99.96%), hydrogen (99.99%) and oxygen (99.995%). Argon and hydrogen were passing through an additional purifier. For optical measurements Perkin-Elmer spectrophotometers were used. X-ray diffractometry and Reflection of High Energy Electron Diffraction methods were used for

structural studies.

3. Experimental Results and Discussions

Two kinds of processes have been applied during our work: hydrogen reduction of MoO_2Cl_2 and pyrolytical decomposition of $\text{W}(\text{CO})_6$ in the presence of oxygen. By changing the temperature from 550 °C up to 710 °C and H_2 concentration (the presented here results are for hydrogen content of 140 cc/min) we obtained films consisting either of pure MoO_2 or of MoO_2 : Mo , the latest in a volume fraction ratio, depending the process parameters - temperature and hydrogen content. By pyrolytical decomposition of $\text{W}(\text{CO})_6$ in the presence of O_2 we obtained films, consisting of different oxides. Details about the exact data for the process parameters are given elsewhere [8]. After annealing in hydrogen atmosphere at temperatures from 550 °C to 750 °C films change their phase structure. By changing the oxygen content and the annealing temperature we have optimized the optical performance of the films, their reflectance in the visible and the infrared range and a_s/e_t ratio [8]. Using the formula for a_s and e_t (given below), on the base of the optimized reflectance the following values were obtained: $a_s = 0.89$ (without antireflecting coating) and $e_t = 0.28$ (calculated for blackbody radiation spectrum at 500°C). In the present work we studied the phase structure and follow how it was changing in result of the annealing temperature when the oxygen content is 1 cc/min. The latest value was defined during the optimization of the reflectance [8].

The results from the phase structural studies of the black Mo and black W thin films are presented in the following tables and figures: In Table 1 d-spacings and intensities for the observed lines in the X-ray diffraction patterns of black molybdenum film are presented. The film is deposited at substrate temperature of 610°C. The thickness of the film is 0.5 μm .

As it is seen from Table 1 the film consists of MoO_2 and no other phases are presented. The experimental data are compared to the theoretical ones for powder sample of monoclinic MO_2 [9]. If the substrate temperature of the is increased to 630°C the energy is enough for MoO_2Cl_2 to be reduced to MoO_2 and for further partial reduction of MoO_2 to pure Mo. This can be seen in Table 2. As it is seen from the table, the most intensive Mo line appears in the diffraction pattern. When the temperature is increased to 670°C, the hydrogen reduction of MoO_2Cl_2 goes to almost a completion and film consists mainly of Mo and a small fraction of MoO_2 , which is presented in the diffraction pattern by only the strongest line, corresponding to d-spacing

Table 1 X-ray diffraction analysis data for Mo films, deposited at 610 °C and H₂ of 140 cc/min.

Crystal phase	h k l	Expected results			Experimentally observed results		
		I/I ₀	d(Å)	2θ	2θ	d(Å)	I/I ₀
MoO ₂	110	100	3.41	26.10	26	3.42	100
MoO ₂	020	85	2.42	37.12	37.12	2.42	28
MoO ₂	222	80	1.70	53.74	53.70	1.70	24
MoO ₂	313	35	1.52	60.80	60.70	1.52	7
MoO ₂	131	50	1.39	66.92	66.92	1.39	3
MoO ₂	133	30	1.20	79.64	79.64	1.20	3

Table 2. X-ray diffraction analysis data for black Mo film, deposited at 630 °C and H₂ of 140 cc/min.

Crystal phase	h k l	Expected results			Experimentally observed results		
		I/I ₀	d(Å)	2θ	2θ	d(Å)	I/I ₀
MoO ₂	001	19	4.78	18.54	18.4	4.8	25
MoO ₂	110	100	3.41	26.1	25.9	3.4	8
MoO ₂	020	85	2.42	37.12	37.2	2.42	100
Mo	110	100	2.225	40.5	40.4	2.23	88*
MoO ₂	310	25	1.54	60.2	59	1.56	9
MoO ₂	221	25	1.46	63.54	64	1.45	5
MoO ₂	113	25	1.287	72.74	74	1.28	10

* The Mo line intensity is compared to the intensity of the strongest MoO₂ line observed.

of 2.42 Å. This can be seen in table 3.

For the obtained samples we measured the hemispherical reflectance in the solar energy region (0.3 - 2.5 μm) and near-normal reflectance in the infrared (2.5 - 15 μm). On the basis of the reflectance curves we calculated the solar absorptance a_s and the thermal emittance e_t of the black Mo films. The following formula were used:

$$a_s = \frac{\int [1 - R(\lambda)] \phi(\lambda) d\lambda}{\int \phi(\lambda) d\lambda}, \quad (1)$$

Table 3. X-ray diffraction analysis data for black Mo film,
deposited at 670 °C and H of 140 cc/min.

Crystal phase	h k l	Expected data			Experiment. observed data		
		I/I ₀	d, Å	2θ	2θ	d, Å	I/I ₀
MoO ₂	200	100	2.43	36.9	36.6	2.43	6 ⁺
Mo	110	100	2.225	40.5	40.5	2.225	100
Mo	200	21	1.57	58.6	58.9	1.57	6
Mo	211	39	1.28	73.7	73.9	1.28	20
Mo	220	11	1.11	86.6	88	1.11	4
Mo	310	17	0.99	101.4	101.9	0.99	2
Mo	222	7	0.91	116.0	116.4	0.91	3
Mo	321	26	0.84	132.6	133.2	0.84	6

⁺MoO₂ line intensity is compared to the 100 Mo line intensity.

where R is the reflectance measured in the range (0.35 - 2.5 μm), $\phi(\lambda)$ is the standard solar spectrum function [10]:

$$e_t = \frac{\int [1 - R(\lambda, \theta=7^\circ)] e_{bb}(\lambda, T) d\lambda}{\int e_{bb}(\lambda, T) d\lambda}, \quad (2)$$

where R is the reflectance, e_{bb} is the black body distribution spectrum [11].

With an antireflective coating of Si₃N₄ with thickness of 1125 Å black Mo coatings reach solar absorptance $a_s = 0.92$ and thermal emittance calculated for 500 °C black body temperature spectrum $e_{t=500} = 0.28$ for samples obtained at temperature of 670 °C and $a_s = 0.95$, $e_t = 0.33$ for samples obtained at temperature 610 °C. For the black tungsten thin films obtained as explain above, we studied the phase structure. For an as-deposited W film results are presented on figure 1. We see from the figure that the film structure consists of mixture of different oxides - WO₂, WO₃ and W₂O. We note, that in this temperature range (400 °C) WO₃ crystalline phase starts to grow in the film structure. At lower temperatures, especially below 300 °C the films grow in an amorphous phase. Other authors, studying W oxide films deposition by other technics note, that 400 °C as an annealing temperature leads to the same effect, namely forming of WO₃ crystalline phase [13]. As deposited films were annealed in H₂ atmosphere at 500 °C for 5 min (the time duration was defined in result of the optimization of the optical performance). The results from the structural studies for such a film are presented on figure 2. We see, that WO₃ lines have smaller

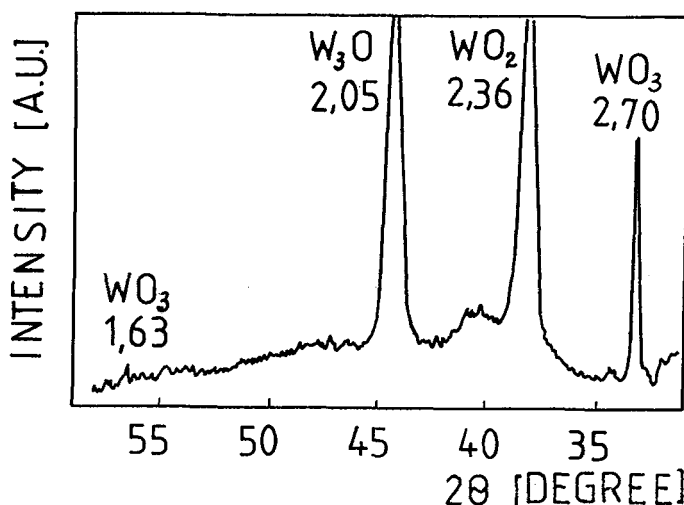


Fig.1. X-ray diffractogram for W oxide film, as-deposited by CVD of $W(CO)_6$ at 400 °C in the presence of 1 cc/min oxygen flow.

intensity and new WO_2 lines appear. Going to higher annealing temperatures WO_3 lines disappear and pure W line appears, which is an evidence for a higher degree of reduction during the annealing. Results of X-ray

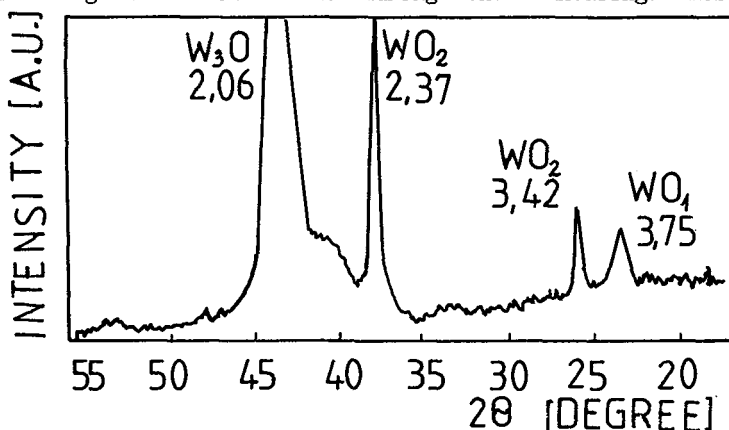


Fig.2. X-ray diffractogram for W oxide film, deposited at 400 °C, 1 cc/min O_2 and additionally annealed at 550 °C for 5 min.

diffraction analysis of films, annealed at 600 °C are shown in Fig.3. Besides oxides phases in the film structure, pure W crystalline phase starts to be formed and the strongest W line for d-spacing 2.22 Å appears in the diffractogram. Increasing the annealing temperature to 750 °C resulted in film with phase structure, presented on figure 4. From the figure is seen that the pure W line intensity at d-spacing of 2.22 Å increases considerably

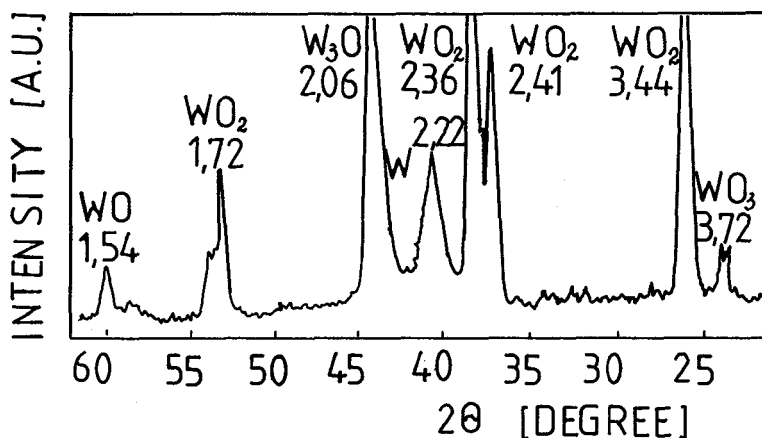


Fig.3. X-ray diffractogram for W oxide film, deposited at 400 °C, 1 cc/min O₂ and additionally annealed at 600 °C for 5 min.

and a new W line appears in the diffraction pattern. Evidently, at higher temperatures the reduction process becomes stronger, the energy is higher

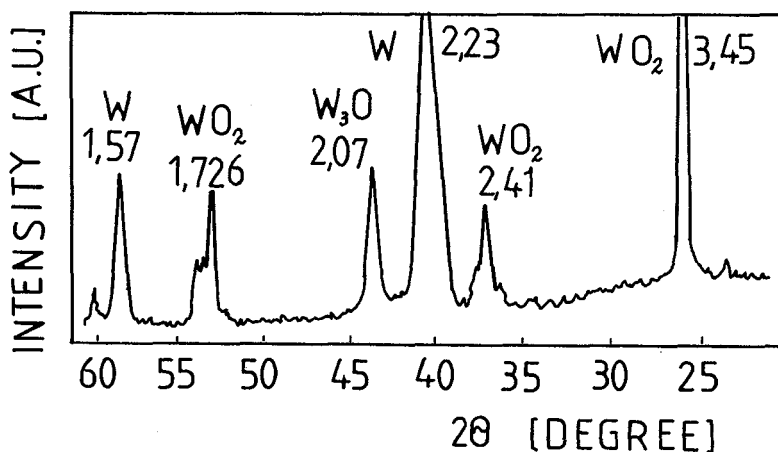


Fig.4. X-ray diffractogram for W oxide film, deposited at 400 °C, 1 cc/min O₂ and additionally annealed at 750 °C for 5 min.

to break up the oxide molecule, hydrogen connects with the oxygen, forms water which leaves the film.

From the X-ray analysis results we see, that WO₃ is possibly to grow in a range of about 500 °C. This temperature is used by other authors for obtaining of WO₃ films [13]. We find that it would not be possible to obtain easily a WO₃ film by "in situ" CVD-process. It is possible to obtain WO₃ films if pure W films, deposited by CVD process are annealed in O₂ rich

atmosphere at 500 - 600 °C for several hours. In order to obtain WO_3 films we use the following processes: First, we deposited W films on glass substrates by CVD pyrolytical decomposition of $W(CO)_6$ in argon atmosphere and further the films were heated at 500 °C in oxygen containing atmosphere for 4 hours. In result WO_3 was formed, films were transferred from metally looking to highly transparent ones. Some films were deposited on precoted with In_2O_3 glass substrates. We measured the transmittance of the films in the solar spectrum region and the results showed that films have about 75-80% transmittance in this region. On figure 5 the results for two films are presented, one obtained on bare glass, and the other on precoted with $In_2O_3:Sn$ glass substrate. The two films have similar transmittances. The precoting with such a film is important for application of WO_3 in "smart windows" multilayered systems. We studied the structure of the films obtained in this way, using the RHEED method. The results show that all samples have structures of WO_3 . On figure 6 we see the electrtonogram of a film, obtained on precoted with $In_2O_3:Sn$ substrate.

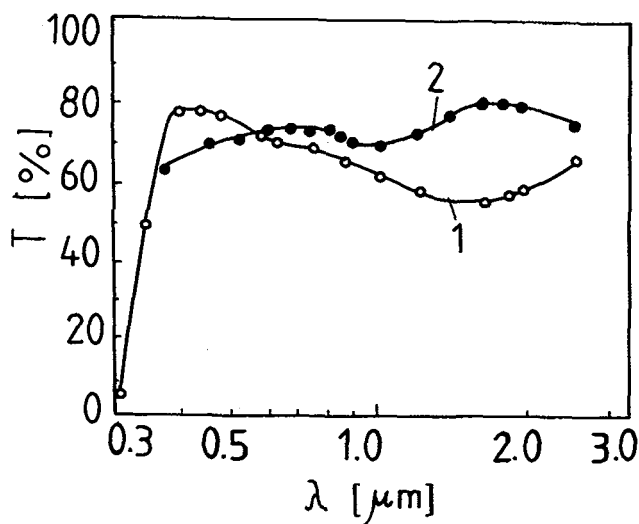


Fig.5. Spectral transmittance of WO_3 obtained on bare glass (1) and precoted with $In_2O_3:Sn$ glass substrate (2)

The reflexes, corresponding to d-spacings 3.78 Å, 3.27 Å, 2.71 Å, 2.44 Å, 2.14 Å were found on the presented electronogram.

In conclusion, we would like to emphasize that transition metal oxides structures is possible to be obtained using the CVD method and they are

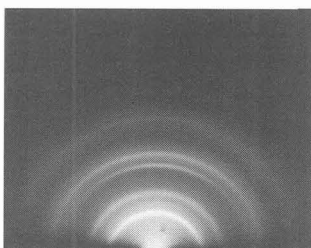


Fig 6. RHEED patern of WO_3 thin film obtained
on $\text{In}_2\text{O}_3:\text{Sn}$ glass substrate

prospective solar energy materials. Studying the correlation between process parameters and film structures we can obtain thin film materials for solar energy utilization.

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