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Effect of substrate temperature and film thickness on the surface structure of some thin amorphous films of MoO_3 studied by X-ray photoelectron spectroscopy (ESCA)

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X-ray photoelectron spectroscopy (XPS) core level spectra of MoO_3 substoichiometric amorphous thin films in the thickness range 100 to 670 nm were studied as a function of thickness. Some samples 500 nm thick were studied for different substrate temperatures in the range 293 to 543 K. It was observed that with the increase of thickness of the samples no change in the electron spectrum was observed in the material. Under vacuum conditions, MoO_3 turned blue when the substrate temperature was higher than 373 K. XPS spectra supported the formation of the Mo^{5+} oxidation state in the blue samples. Blue coloration was observed after heating in vacuum and this was attributed to an internal electron transfer from oxygen to metallic orbitals by thermal ionization creating an Mo^{5+} oxidation state.

1. Introduction

X-ray photoelectron spetroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA) is a useful technique to follow the electron changes in both core and valence band spectra in transition metal oxides. X-ray photoelectron spectroscopy is widely used in surface analysis to conduct depth profiling of chemical composition. The ability of the XPS method to distinguish between the different oxidation states allows an efficient study of these changes with most of such studies concerning the core levels. Photoemission studies of the valence and core levels of molybdenum trioxide are of great interest and the need for such studies is further increased by the fact that reliable band calculations are presently not available for this oxide because of its complex crystalline structure. A variety of methods has been advanced to described these phenomena. Earlier models postulated the trapping of electrons at oxygen vacancies [1–3]. There have been previous XPS studies of photochromism phenomena in amorphous thin films of MoO_3 [4–6].

Firment and co-workers [7, 8] studied the surface properties of stoichiometric and oxygen deficient crystalline MoO_3 by XPS and reported that heating in a vacuum induced some reduction of the MoO_3 surface whereby some Mo^{6+} ions were reduced to Mo^{5+} and there was diffusion between the surface region and the bulk. Additionally, bombardment with electrons or ions may alter the surface chemistry.

Werfel and Suoninen [9] studied the electronic structure of crystalline molybdenum oxides by a photoelectron study and reported that blue-coloured MoO_3 samples contained trapped electrons at oxygen vacancies. The same phenomenon has been observed by Rabalais *et al.* [4].

Anwar and co-workers have studied the optical and electron spin resonance (ESR) properties of this material [10, 11]. It has been observed that the structure of amorphous thin films of MoO_3 is substantially different from that of the single crystal, partly because of the substoichiometric composition of the films. In addition, the properties of the thin layers vary with the preparation techniques employed. The decrease in optical gap with both the rise of substrate temperature and also with increasing thickness has been observed. The ESR signal intensity was found to have increased with both increasing thickness and substrate temperature. It has also been observed that MoO_3 forms substoichiometric oxides upon heating in vacuum.

In this work we have used XPS core level measurements to analyse the changes in the oxidation states of the transition metal oxide which occurred during heating in vacuum. The effect of substrate temperature and film thickness on the surface structure and oxidation state is observed by the XPS technique.

2. Experimental work

2.1. Sample fabrication technique

The amorphous thin films used in this study were prepared by vacuum evaporation of high-purity MoO_3 (99.9%). This oxide was evaporated from an electrically heated molybdenum boat in a Balzers BA510 coating unit. The oxides were deposited on to clean Corning 7059 glass substrates at a pressure of 6×10^{-6} torr. The film thicknesses of between 100 and 670 nm were attained at a deposition rate of 0.75 nm sec^{-1} with the substrates at room temperature.

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Some 500 nm thick samples were fabricated with the substrates in the temperature range 293 to 543 K. The substrates were heated to the required temperature by a heater mounted at the top of the bell jar. The thickness of the films was monitored using a quartz crystal monitor and finally the exact film thickness was determined by multiple beam interferometry [12].

Freshly evaporated samples at room temperature were transparent but the coloration of the samples changed from white to blue as the deposition substrate temperature was changed from room temperature to 543 K. X-ray diffraction studies on freshly-evaporated thin films of MoO_3 showed that the films were amorphous when deposited on substrates below 523 K, and at 523 K or above the films were tending towards a crystalline structure.

2.2. XPS measurements

Photoelectron spectra were recorded with a Kratos ES300 electron spectrometer using Al$K\alpha$ (1486.6 eV) radiation. Samples were analysed as soon as possible after evaporation. In this way surface contamination was kept to a minimum and the need for ion etching, known to cause changes in surface chemistry [7, 8], was avoided. The instrumental resolution was ≈ 0.9 eV with a slit width of ≈ 0.17 cm. Samples were maintained at ambient temperature and a pressure of 5×10^{-8} torr throughout the investigation.

The binding energy scale was calibrated by assigning a value of 284.6 eV to the C(1s) signal as suggested by Wagner *et al.* [13]. XPS core level emission peak areas were obtained by investigation of the spectra after assignment of a linear base line.

3. Results

Fig. 1 shows the XPS core level Mo(3d) spectra of MoO_3 for seven different film thicknesses in the range 100 to 760 nm with the substrates at room temperature during the deposition. Fig. 2 shows the core level O(1s) spectra of MoO_3 for seven different thicknesses with substrates at room temperature. The XPS core level Mo(3d) spectra of MoO_3 at four different substrate temperatures (293 to 543 K) are shown in Fig. 3. No appreciable change in the binding energy is observed with increasing thickness as shown in Fig. 1. The MoO_3 spectrum exhibits the characteristic $3d_{5/2}$ and $3d_{3/2}$ doublet caused by the spin-orbital coupling [14]. The binding energy and spin-orbit splitting (ΔMo3d) are in good agreement with the

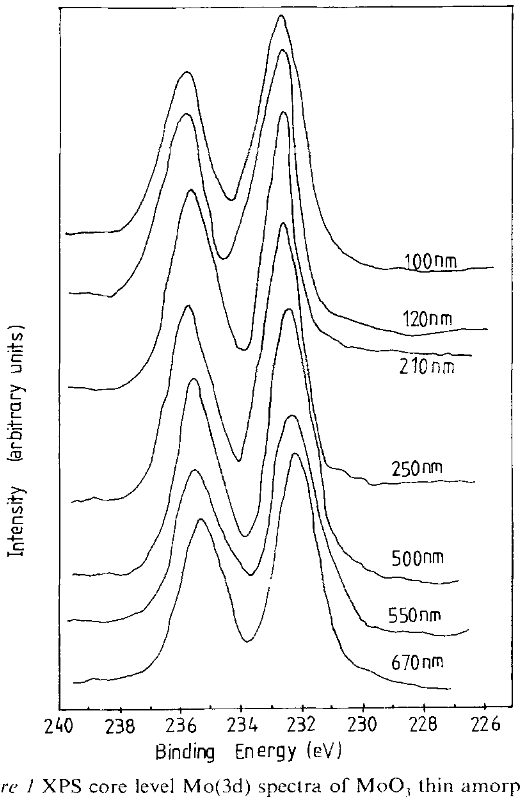

Figure 1 XPS core level Mo(3d) spectra of MoO_3 thin amorphous films of various thicknesses.

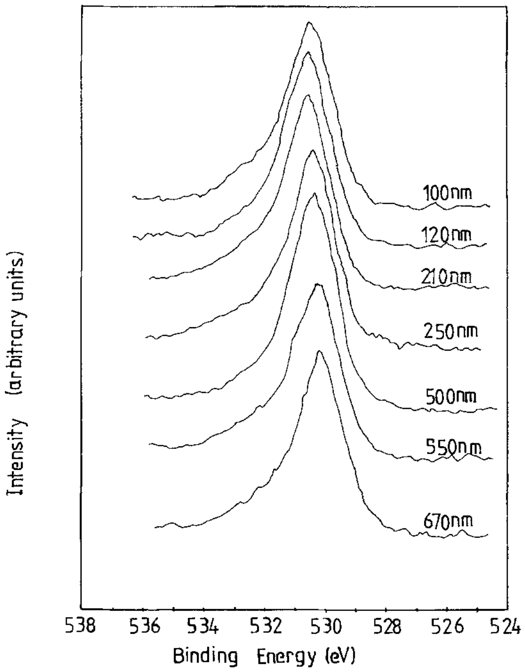

Figure 2 XPS core level O(1s) spectra of MoO_3 amorphous thin films of various thicknesses.

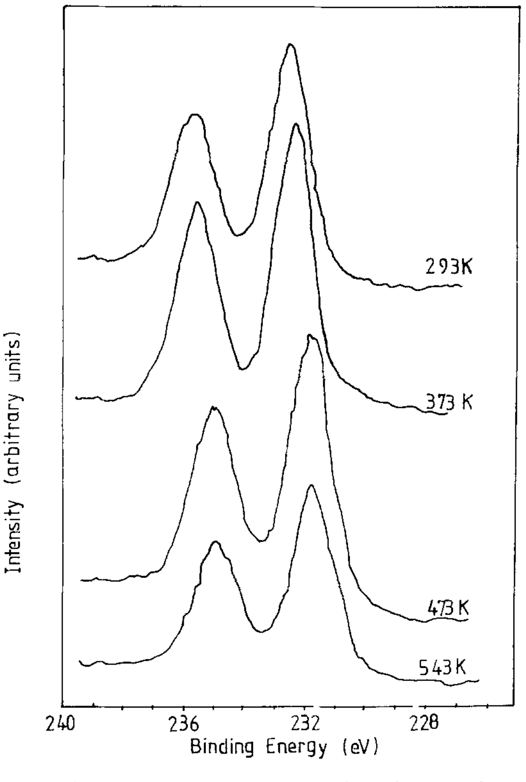

Figure 3 XPS core level Mo(3d) spectra of MoO_3 amorphous thin films deposited at various substrate temperatures.

TABLE I Photoelectron binding energies of MoO_3 and O(1s) core electrons with increasing sample thickness

Sample thickness (nm)	$Mo3d_{3/2}$ (eV)	$Mo3d_{5/2}$ (eV)	ΔMo3d (eV)	O(1s) (eV)
100	235.80	232.60	3.20	530.60
120	235.75	232.55	3.20	530.58
210	235.62	232.45	3.17	530.58
250	235.71	232.54	3.17	530.48
500	235.55	232.35	3.20	530.40
550	235.53	232.21	3.22	530.35
670	235.40	232.20	3.20	530.30

values reported for MoO_3 by other workers [5, 7, 9, 13, 15, 16].

The line shape of the MoO_3 doublet ($3d_{3/2}$, $3d_{5/2}$) is gaussian and the *d* intensity ratio is 2:3. The MoO_3 doublet is separated by 3.17 to 3.22 eV. The positions of the Mo(3d) lines are those expected for Mo^{6+} ions as in MoO_3 [5, 7, 16]. At higher thicknesses there is a slight shift in position towards lower binding energy. The measurement of the peak areas of the O(1s) and Mo(3d) XPS peaks gave a ratio at room temperature of 0.71. The O(1s) binding energy is found to be 530.45 ± 0.15 eV [5, 15, 17]. Table I shows the photoelectron binding energies of Mo(3d) and O(1s) core electrons with increasing thickness. A comparison of the Mo(3d) and O(1s) binding energies as mentioned by several other authors is shown in Table II.

In Fig. 3 the top line provides the reference point and is obtained with the substrate at room temperature. The position of the Mo(3d) line at room temperature is that expected for Mo^{6+} as in MoO_3. As the temperature of the substrates is increased the position of the Mo(3d) lines shifts towards Mo^{5+}. At substrate temperature 543 K, the shift in the Mo(3d) line position is in excellent agreement with the line position of Mo^{5+} [15, 16]. Table III shows the photoelectron binding energies of Mo(3d) core electrons with increasing substrate temperatures. A comparison of photoelectron binding energies of Mo(3d) core electrons of two oxidation states in thin amorphous films of MoO_3 as mentioned by several authors is shown in Table IV.

4. Discussion

The photoelectron spectral results mentioned in this work show the following main results.

1. The positions of the Mo(3d) lines are as expected for Mo^{6+} as in MoO_3. A slight shift in the positions of the Mo(3d) lines towards lower photoelectron binding energies at higher thickness is also observed.

2. The position of the Mo(3d) lines shift towards the lower photoelectron binding energies which are assigned to the Mo^{5+} state for the blue coloured samples at higher substrate temperatures.

A reasonable explanation is given in the following. Molybdenum trioxide is an insulator with an unusual layer structure and exhibits several interesting physical properties. MoO_3 is a white powder, which loses oxygen when heated in vacuum and readily changes to lower oxidation states. The films evaporated on substrates at room temperature look white in colour and are reasonably transparent. The colour of the samples changes to blue when the substrates are heated above 373 K, and at 543 K the colour of the samples is dark blue.

Measurements of XPS core level spectra of MoO_3 with increasing thickness reveal that the value of binding energy is almost constant in the thinner samples, but although there is a slight decrease in binding energy at higher thicknesses, these binding energies still have the values assigned to the Mo^{6+} oxidation state. This slight change in binding energy may be attributed to instrumental variation. An alternative explanation for this decrease in binding energy may be the presence of oxygen vacancies due to heating in vacuum. When the thickness of the samples is increased, the concentration of oxygen vacancies, i.e. positively charged structural defects, is increased. The degree of localization of electrons increases with the increase of cation concentration, thereby increasing the number of donor centres. A large concentration of donor levels may lower the binding energy of the electrons.

The substrate temperature has a considerable effect on the optical and electron spin resonance (ESR) properties of MoO_3 as reported by Anwar *et al.* [10, 11]. The binding energies for the blue samples having a substrate temperature 473 K or above are within the range 231.7 to 231.8 eV for $Mo3d_{5/2}$ and 234.8 to 234.9 eV for $Mo3d_{3/2}$. The spin-orbit splitting is 3.18 eV and the observed intensity ratio $3d_{5/2}/3d_{3/2}$ is 1.5. On heating the substrates in vacuum at 473 K or above, the Mo(3d) doublet appears at lower binding energies, and indicates the formation of a molybdenum species of lower valency. The binding energy of the newly formed molybdenum oxidation state is in excellent agreement with the binding energy assigned to the Mo^{5+} oxidation state. The blue coloured films exhibit a small band near the Fermi level [5]. We attribute this

TABLE II A comparison of photoelectron binding energies of MoO_3 and O(1s) core electrons as mentioned by several authors

$Mo3d_{3/2}$ (eV)	$Mo3d_{5/2}$ (eV)	ΔMo3d (eV)	O(1s) (eV)	Other workers
235.85	232.65	3.2	529.50–530.50	Wagner *et al.* [13]
235.80	232.60	3.2	530.40 ± 0.1	Fleisch and Mains [15]
235.70	232.50	3.2	530.30	Colton *et al.* [5]
235.10	232.00	3.1	–	[16]
235.80	232.70	3.1	–	Baba and Sasaki [19]
235.50	232.20	3.5	530.30	Kim *et al.* [20]
235.40–235.80	232.20–232.60	3.17–3.22	530.45 ± 0.15	Present work

TABLE III The photoelectron binding energies of Mo(3d) core electrons for increasing substrate temperatues

Substrate temperature (K)	Oxidation states	$Mo(3d)_{5/2}$ (eV)	$Mo(3d)_{3/2}$ (eV)
293	6+	235.80	232.60
373	6+	235.61	232.42
473	5+	234.95	231.98
543	5+	234.88	231.70

band to electrons trapped in positively charged anion vacancies within the film structure. If we consider MoO_3 to be ionic, i.e. formed from Mo^{6+} and O^{2-} ions, the valence band would consist of oxygen 2p states and the conduction band would consist of empty 4d and 5s states [18]. The transition from oxygen 2p to an empty Mo^{6+} 4d level will give rise to the incorporation of some lower valency Mo^{5+} ions in the lattice. Our results are consistent with some authors [5, 15, 16]. These XPS results are in excellent agreement with our ESR results [9] in which formation of Mo^{5+} ions is inferred from the rise of substrate deposition temperature.

5. Conclusions

1. The slight decrease in binding energy with increasing thickness of the samples whose substrates were at room temperature during deposition, may be either due to instrumental error or due to the increasing concentration of donor levels in these samples.

2. Heating the substrates in vacuum at 473 K or above results in the blue coloration of the samples and the appearance of the Mo(3d) doublet at lower binding energy, indicating the formation of molybdenum species of lower oxidation state, i.e. Mo^{5+}. This new oxidation state is formed from the electron transfer from oxygen 2p to the molybdenum 4d level.

TABLE IV A comparison of photoelectron binding energies of Mo(3d) core level electrons of two oxidation states in amorphous thin films of MoO_3 as mentioned by several authors

Authors	Oxidation states of molybdenum	$Mo(3d)_{3/2}$ (eV)	$Mo(3d)_{5/2}$ (eV)
Fleisch and Mains [15]	6+	235.80	232.60
	5+	234.60	231.40
[16]	6+	235.10	232.00
	5+	234.00	230.00
Present authors	6+	235.80	232.60
	5+	234.88	231.70

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