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A study of the infrared absorption spectra of thin amorphous films of molybdenum trioxide

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The spectra of thin amorphous films of MoO_3 deposited by vacuum evaporation have been studied within the spectral range 4000–400 cm^{-1} by the Fourier transform infrared technique. Some samples in the thickness range 100 to 400 nm were investigated at room temperature. Four samples were investigated in the substrate deposition temperature range 293 to 543 K. Some samples were annealed in vacuum in the temperature range 473 to 673 K and their IR spectra were recorded as soon as the samples were cooled to room temperature. It has been observed that annealing of the samples at 473 K or above and also heating the substrates in the temperature range 473 K or above, results in the formation of molybdenum species of lower oxidation state than the normal Mo(VI), i.e. Mo(V). This new oxidation state is formed by electron transfer from the oxygen 2p to the molybdenum 4d level.

1. Introduction

Fourier transform infrared (IR) spectroscopy is a well-known technique for the study of surface features of materials and is indeed one of the few methods that allow direct examination of absorbed molecules on a solid surface. Molybdenum oxide has several important industrial applications at relatively high temperature as catalysts and thus structural and spectroscopic data are of great value. The study of molybdenum is complicated by the fact that there are two stoichiometric oxides (MoO_2 and MoO_3) and a range of intermediate oxides.

Molybdenum has an interesting layer structure. Py and Maschke [1] have studied the intra-layer and inter-layer contributions to the lattice vibrations in MoO_3 and concluded that MoO_3 can be considered as a layered material in which the single layers are built up from moderately coupled chains. However, the characterization of the lattice vibrations in terms of internal or external modes is not possible for all the modes.

A number of investigations have been made on the infrared properties of MoO_3 [2–9]. Gratton *et al.* [10] have studied the IR emission spectroscopy applied to the oxidation of molybdenum and concluded that the crystal structure on the oxidized surface forms at an advanced stage of the oxidation, when the layer of the oxide is thick. The thickness of a MoO_3 layer modifies the band intensity and band resolution. It has been shown that the quality of an emission spectrum increases as the layer thickness decreases. Most of the previous work on molybdenum trioxide and its sub-oxides was restricted to X-ray diffraction studies. Khilborg [11] stated that different oxides exhibit considerable distortion, which is interpreted as being due to off-centre displacement of the metal atoms. This effect might be associated with variation in the valence state of the metal atom within the basic structure.

Anwar *et al.* [12–15] have studied the optical, X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) and DC electrical properties of MoO_3 thin films and concluded that substrate temperature during film deposition has a considerable effect on these properties. It has been observed that the optical band gap is decreased by increasing the substrate temperature. It has also been observed that MoO_3 forms sub-stoichiometric oxides upon heating in vacuum. XPS and ESR properties have revealed that heating the substrates in vacuum at 473 K or above results in the blue colouration of the samples and the formation of molybdenum species of lower oxidation state. It has been observed from the results of electrical measurements that upon heating the substrates in vacuum at 473 K or above a defect band is formed near the Fermi level and is associated with the colouration of the samples and the formation of a reduced state species. The greatly enhanced conductivity in blue samples was due to the higher mobility of electrons in the defect band and in the conduction band.

In this work we have studied the FTIR spectra of MoO_3 as a function of substrate temperature, film thickness and annealing. The results obtained are analysed in terms of current theory.

2. Experimental work

The amorphous thin films used in this study were prepared by vacuum evaporation of high purity MoO_3. This oxide was evaporated from an electrically heated molybdenum boat in a Balzers BA 510 coating unit and was deposited on to clean silicon wafer sub-

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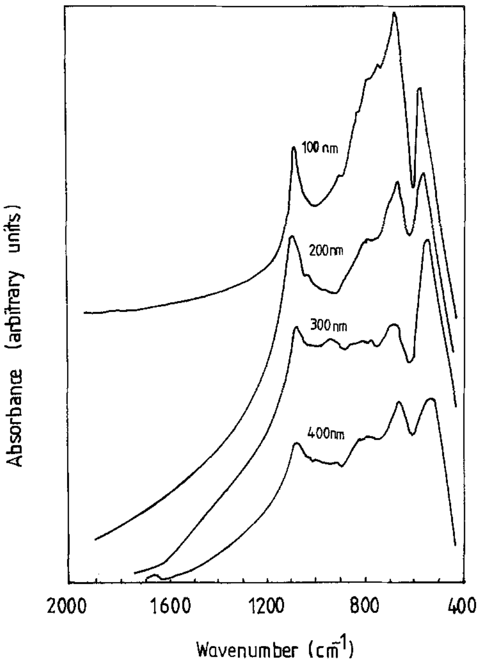

Figure 1 FTIR spectra of four samples in the thickness range 100 to 400 nm with substrates at room temperature.

strates at a pressure of 6×10^{-6} torr. Film thickness in the range 100 to 400 nm was attained at a deposition rate of 0.75 nm $\sec^{-1}$. Some 100 nm thick samples were fabricated with substrates in the temperature range 293 to 543 K. The thickness of the samples was monitored by using a quartz crystal monitor and finally the exact film thickness was determined by multiple beam interferometry.

Some samples 400 nm thick were annealed in the temperature range 473 to 673 K at a pressure of 10^{-3} torr for 2 h and allowed to cool down at a rate of 2° C $\min^{-1}$. IR spectra for the samples were recorded immediately after the films were cooled to room temperature in a Perkin-Elmer 1710 Fourier transform IR spectrometer over the range 4000–400 cm^{-1}. An average of 10 scans was automatically obtained by the spectrometer.

3. Results

Molybdenum trioxide gives absorption bands in the IR (4000–200 cm^{-1}) region. The majority of the molecular vibrational frequencies are present in this region. At the moment we are primarily interested in the 2280 to 620 cm^{-1} range. Figure 1 presents the IR spectra of four samples in the thickness range 100 to 400 nm. Table I lists the six important IR bands contained within the frequency range 1620 to 620 cm^{-1}. Figure 2 shows the IR spectra of four samples, each having thickness 100 nm and for substrate deposition temperature in the range 293 to 543 K. Table II shows the eight important absorption bands within the frequency range 2280 to 620 cm^{-1}. Figure 3 gives the IR spectra of four samples each having thickness 400 nm and annealed in the temperature range 473 to 673 K. Eight bands contained in the frequency range 2280 to 620 cm^{-1} are listed in Table III.

TABLE I Infrared peak positions of MoO_3 thin films in the thickness range 100 to 400 nm

Film thickness (nm)	Positions of IR bands (cm^{-1})					
	1	2	3	4	5	6
100	620 (s)	740 (sh)	800 (sh)	910 (sh)	1020 (s)	–
200	620 (s)	760 (w)	800 (sh)	910 (w)	1020 (w)	–
300	622 (s)	760 (w)	800 (sh)	890 (w)	1020 (w)	–
400	620 (s)	760 (w)	820 (sh)	900 (w)	1020 (w)	1620 (w)

sh = shoulder, w = weak, s = strong.

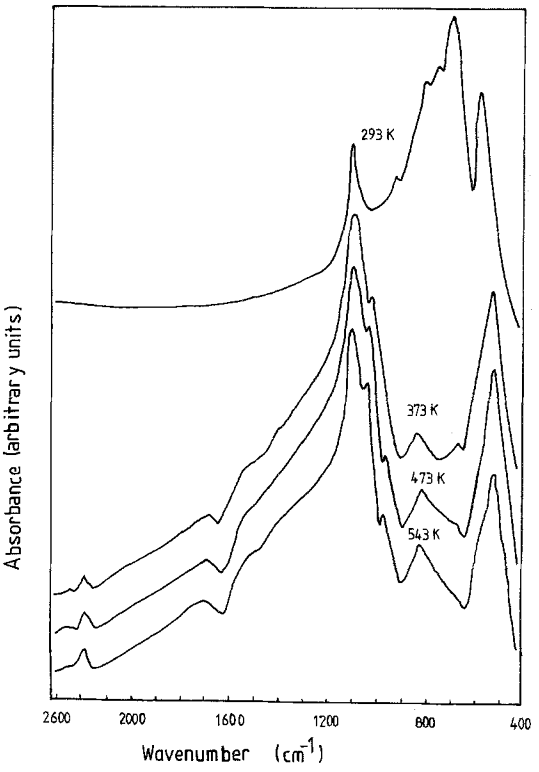

Figure 2 FTIR spectra of 100 nm thick samples in the substrate deposition temperature range 293 to 543 K.

4. Discussion

In molybdenum trioxide each molybdenum atom coordinates six oxygen atoms to form MoO_6 octahedra which are joined by sharing edges to form zig-zag shaped rows. A very slight shift in the position of some bands is obtained and additional bands are detected in some samples having higher substrate deposition temperatures and in annealed samples.

TABLE II Infrared peak positions of MoO_3 thin films 100 nm thick in the substrate deposition temperature range 293 to 543 K

Substrate deposition temperature (K)	Positions of IR bands (cm^{-1})							
	1	2	3	4	5	6	7	8
293	620 (s)	740 (sh)	800 (sh)	910 (sh)	–	1020 (s)	–	–
373	630 (vw)	740 (sh)	–	900 (s)	–	1020 (sh)	1620 (vw)	2280 (vw)
473	630 (w)	–	–	890 (s)	960 (sh)	1020 (sh)	1620 (w)	2240 (vw)
543	620 (s)	–	–	880 (s)	960 (sh)	1020 (sh)	1620 (w)	2240 (w)

sh = shoulder; w = weak; vs = very weak; s = strong.

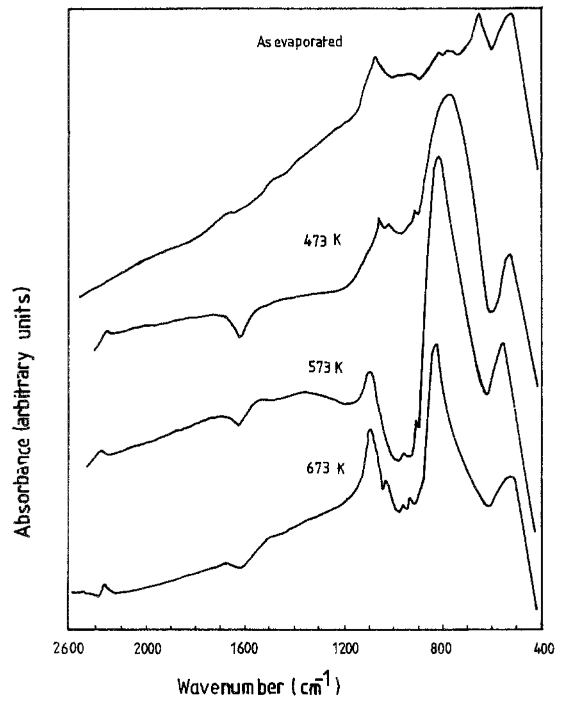

Figure 3 FTIR spectra of 400 nm thick samples annealed in the temperature range 473 to 673 K.

The absorption band at 600–630 cm^{-1} is observed in all the samples with a slight shift in the positions of this band from sample to sample. The band is attributed by Hanafi *et al.* [16] to the first harmonic of the value 307 obtained by Barraclough *et al.* [17], (307 × 2). The band at 740–760 cm^{-1} is obtained in the samples with increasing thickness having substrates at room temperature and in the samples deposited on to a substrate at 373 K. This band disappears in the samples having substrate deposition temperature 473 K or higher and in the samples annealed at 473 K or higher and appears as a shoulder in the thinner samples and becomes weaker in thicker samples. This band may be attributed to the presence of the Mo(VI) species [13]. The absence of this band in the samples having substrate temperature 473 K or above and in the samples annealed at 473 K or above is probably due to the formation of molybdenum species of lower oxidation state i.e. Mo(V) [13, 14].

The band at 800–820 cm^{-1} is present in all the samples of Fig. 1, but disappears in the samples annealed at 473 K or above and in the samples having substrate deposition temperature 473 K or above. This band is attributed by Barraclough *et al.* [17], Hanafi *et al.* [16] and Ismail *et al.* [18] to be due to two different Mo–O–Mo continuous structures. Disappearance of this band in the samples at higher substrate temperatures and in the samples annealed at 473 K or above may be due either to the presence of molybdenum species of lower oxidation state or to the thermal disorder in the samples. The band at 880–920 cm^{-1} is present in all the samples but there is a small shift in some samples. Barraclough *et al.* [17] and Bielan'ski *et al.* [19] attributed this peak to the two different Mo–O–Mo continuous structures in the MoO_3 lattice and pointed out that the MoO_3 structure contains distorted (MoO_6) octahedra in which three of the oxygen atoms are common to the three different octahedra, two oxygen atoms are common to two octahedra and one remains unshared, i.e. bonded only to the molybdenum atom. Heating the substrates in vacuum at 473 K or above and annealing the samples at 473 K or above results in the blue colouration of the samples and the appearance of the band at 960 cm^{-1}, but this band is not present in the samples which are deposited at room temperature and in the sample deposited at 373 K substrate temperature. This band may also be attributed to the formation of molybdenum species of lower oxidation state, i.e. Mo(V). This new oxidation state arises from the electron transfer from the oxygen 2p to the molybdenum 4d level. Our results are consistent with the results given by Hanafi *et al.* [16]. The band at 990–1020 cm^{-1} is present in all the samples of Figs 1, 2 and 3 and is attributed by Gratton *et al.* [10], Bielan'ski *et al.* [19] and Barraclough *et al.* [17] to the stretching vibrations of independent Mo–O groups in the MoO_3 oxide. The bands at 1620 cm^{-1} and 2240–2280 cm^{-1} may be caused by the presence of some lattice imperfections due to heating the substrates and annealing the samples in vacuum.

TABLE III Infrared peak positions of MoO_3 thin films 400 nm thick annealed in the temperature range 473 to 673 K

Annealing temperature (K)	Positions of IR bands (cm^{-1})							
	1	2	3	4	5	6	7	8
As-evaporated	600 (s)	740 (sh)	820 (sh)	900 (w)	–	1020 (sh)	1620 (sh)	–
473	600 (s)	–	–	920 (sh)	960 (w)	1020 (sh)	1620 (s)	2280 (vw)
573	620 (s)	–	–	900 (sh)	960 (sh)	990 (w)	1620 (s)	2280 (vw)
673	620 (s)	–	–	920 (sh)	960 (sh)	990 (w)	1620 (w)	2240 (w)

sh = shoulder; w = weak; vw = very weak; s = strong.

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