Infrared spectra of some thin amorphous films of MoO₃–In₂O₃ deposited by vacuum evaporation

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The infrared absorption spectra of vacuum-evaporated MoO_3–In_2O_3 thin films are reported for a series of films of varying compositions within the spectral range 4000 to 400 cm^{-1} and interpreted in relation to the spectrum of the pure MoO_3 films. The affects of changes in composition, film thickness, substrate deposition temperature and annealing on the absorption bands are observed. In some cases a shift in band frequency is also observed. The gradual increase in ordering and decrease in valency state with increase of annealing temperature is observed in the infrared curves. Some new peaks appear which reveal the presence of a lower valency state in MoO_3. The shift in band frequency may be attributed to the incorporation of Mo(VI) ions in the indium interstitial positions.

1. Introduction

Important information about a semiconductor may be obtained by studying its infrared properties. In turn, semiconducting materials facilitate the study by the fact that samples may be prepared with properties varying over a wide range, e.g. the conductivity can be controlled by adding a small amount of impurity or by varying the temperature. It is, therefore, possible to correlate the infrared properties with other properties of the material by studying different samples under various conditions. The wide interest in semiconducting materials stimulated in part by the practical applications, has led to extensive research, and infrared measurements have become an essential part of the investigation. The study of the infrared properties of evaporated thin films of MoO_3–In_2O_3 prepared by a coevaporation technique [1] helps to elucidate the basic properties of these mixed oxides. Molybdenum trioxide has several important applications at relatively higher temperatures as a catalyst so that the structural and spectroscopic data are of great value. Thus amorphous dielectric films based on MoO_3 are well known as insulators but In_2O_3 is an oxide having high electrical conductivity and sometimes used for transparent electrodes. Kihlborg [2] stated that different oxides exhibit considerable structural 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 atoms within the basic structure. More definite conclusions concerning this subject can be further drawn through the infrared absorption measurements.

A number of investigations have been made on the infrared properties of MoO_3 [3–6] but no results have been published for a range of types of molybdenum oxide or for complex molybdenum oxide films containing other species.

It is known that films of semiconducting indium oxide have high electrical conductivity. Transparent In_2O_3 films of 300 nm thickness have a resistivity of $\approx 10^{-3}$ Ω cm. The relatively high electrical conductivity and very low temperature coefficient of resistivity of In_2O_3 suggest that the lattice energy spectrum of In_2O_3 may include an impurity band, which would determine the metallic character of the conductivity [7]. Anwar et al. [8–9] have studied the optical and XPS spectra of thin films of mixed MoO_3–In_2O_3 oxides and reported that some Mo(VI) ions are incorporated in the indium interstitial positions of the oxygen sublattice of In_2O_3 and the reduction of Mo(VI) ions to the Mo(V) oxidation state at higher annealing temperature has also been observed. An XPS study [9] of MoO_3–In_2O_3 reveals that two kinds of ionic defects are produced in In_2O_3 at higher temperatures.

In the present work we have used the FTIR spectra to analyse the changes in MoO_3–In_2O_3 thin films which occurred at different substrate temperatures, compositions, film thicknesses and annealing temperatures. The results obtained are analysed in terms of current theory.

2. Experimental work

The evaporated amorphous films of MoO_3–In_2O_3 used in this study were deposited on clean silicon wafers held at a pressure of about 6×10^{-6} torr in a Balzers BA 510 coating unit, using the coevaporation technique established by Hogarth and Wright [1]. Molybdenum boats were used for the evaporation of MoO_3 and In_2O_3 oxides. All other techniques used to measure the film thickness, cleaning of the substrates, annealing the samples and infrared measurements are the same as described earlier by Anwar et al. [6].

3. Results

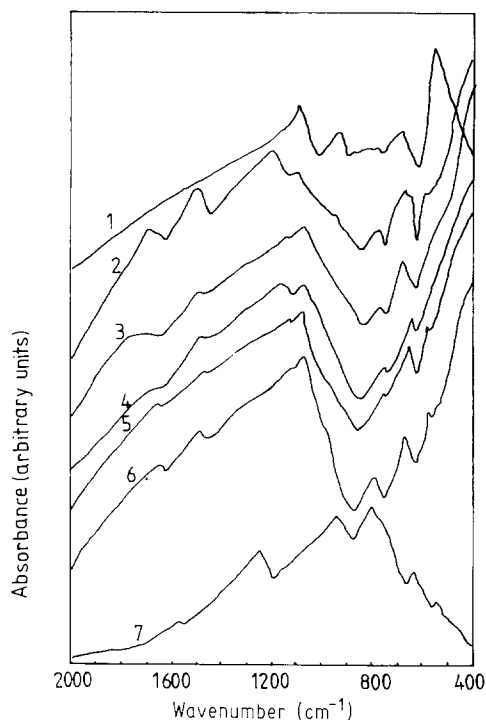Mixed layers of MoO_3–In_2O_3 give absorption bands in the infrared (4000 to 400 cm^{-1}) region. The majority

Figure 1 FTIR spectra of 300 nm thick samples of MoO_3-In_2O_3 of varying compositions (in mol %) with the substrates at room temperature during deposition, (1) 100 MoO_3, (2) 95 MoO_3-5 In_2O_3, (3) 90 MoO_3-10 In_2O_3, (4) 85 MoO_3-15 In_2O_3, (5) 80 MoO_3-20 In_2O_3, (6) 75 MoO_3-25 In_2O_3, (7) 100 In_2O_3.

Figure 2 FTIR spectra of fixed composition (85 mol % MoO_3-15 mol % In_2O_3) samples of various thicknesses, (1) 100 nm, (2) 200 nm, (3) 300 nm, (4) 400 nm.

of the molecular vibrational frequencies are present in this region. A Perkin–Elmer 1710 Fourier-transform infrared spectrometer was used to measure the absorption optical. An average of ten scans was automatically obtained by the spectrometer. Initially we are primarily interested in the 1630 to 544 cm^{-1} range. Fig. 1 shows the IR spectra of amorphous thin layers of MoO_3-In_2O_3 for samples of constant thickness of approximately 300 nm but of different compositions with the substrates at room temperature during deposition. Table I list the nine important IR bands contained within the above range.

Some samples were studied at fixed composition (85 mol % MoO_3-15 mol % In_3O_3) but with various thicknesses with the substrates at room temperature during deposition. Fig. 2 shows the IR spectra of four

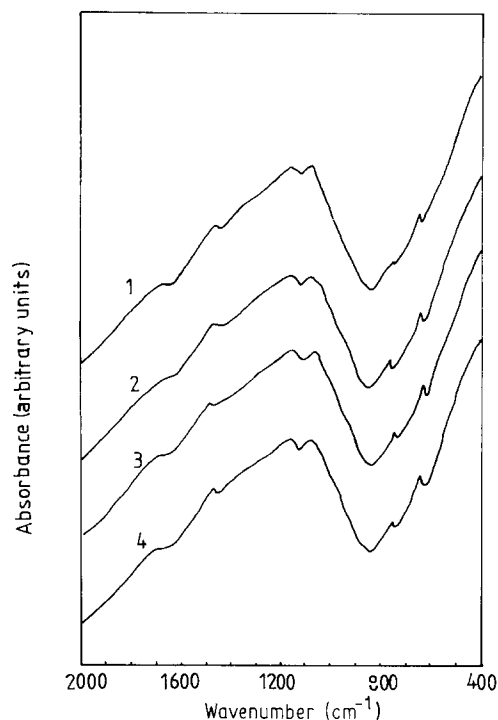samples in the thickness range 100 to 400 nm. Table II shows the six important absorption bands within the frequency range 1630 to 618 cm^{-1}. Fig. 3 shows the IR spectra of four samples of fixed composition (85 mol % MoO_3-15 mol % In_2O_3) each having thickness 200 nm, with the substrate deposition temperature in the range 20 to 270 °C. Table III shows the six IR absorption bands within the frequency range 1630 to 611 cm^{-1} as a function of substrate deposition temperature.

A few samples of fixed compositions (85 mol % MoO_3-15 mol % In_2O_3) and constant thickness of approximately 200 nm, with the substrates at room temperature, were annealed in vacuum for 2 h in the temperature range 200 to 500° C at a pressure of 10^{-3} torr and allowed to cool down at a rate of 2 K min^{-2}. Infrared spectra of samples were recorded immediately after the films were cooled to room temperature.

TABLE I Infrared peak positions of MoO_3-In_2O_3 thin films of thickness 300 nm

Film compositions (mol %)	Positions of IR bands (cm^{-1})								
	1	2	3	4	5	6	7	8	9
100 MoO_3	–	622 (s)	760 (w)	800 (sh)	890 (w)	1020 (w)	–	–	–
(95 MoO_3 -5 In_2O_3)	–	620 (s)	748 (w)	840 (w)	–	–	1120 (sh)	1430 (s)	1630 (s)
(90 MoO_3 -10 In_2O_3)	–	620 (s)	748 (w)	843 (w)	–	–	1120 (sh)	1450 (w)	1630 (w)
(85 MoO_3 -15 In_2O_3)	–	620 (s)	744 (sh)	845 (w)	–	–	1115 (w)	1450 (sh)	1630 (w)
(80 MoO_3 -20 In_2O_3)	576 (vw)	620 (s)	741 (sh)	850 (w)	–	–	1110 (sh)	1450 (vw)	1630 (w)
(75 MoO_3 -25 In_2O_3)	560 (sh)	612 (s)	744 (w)	858 (w)	–	–	1100 (vw)	1450 (w)	1630 (w)
100 In_2O_3	554 (sh)	653 (vw)	–	861 (w)	–	–	1195 (vw)	1550 (w)	–

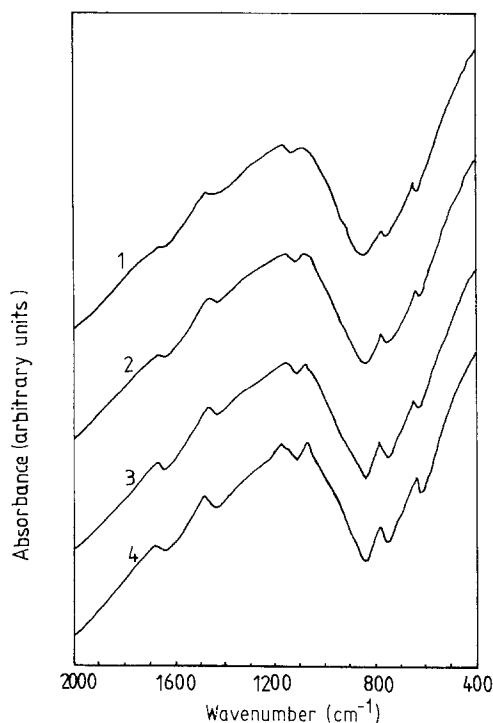sh = shoulder, w = weak, vw = very weak, s = strong

Figure 3 FTIR spectra of 200 nm thick samples (85 mol % MoO₃– 15 mol % In₂O₃) at different substrate deposition temperatures, (1) 20° C, (2) 100° C, (3) 200° C, (4) 270° C.
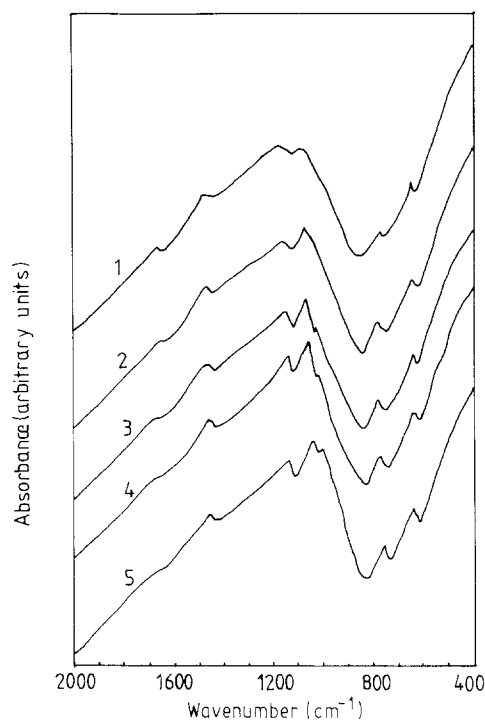

Figure 4 FTIR spectra of 200 nm thick samples (85 mol % MoO₃– 15 mol % In₂O₃) with the substrates at room temperature during deposition and annealed at, (1) As-evaporated, (2) 200° C, (3) 300° C, (4) 400° C, (5) 500° C.

Fig. 4 shows the IR spectra of four samples annealed at various temperatures and the seven absorption bands contained in the frequency range 1630 to 604 cm^{-1} are listed in Table IV.

4. Discussion

An obvious way of analysing the chemical nature of the films is to postulate the presence of possible molecular-like grouping of atoms within the solid and to use their vibrational spectra as a first approximation to the infrared spectra of the films. In the present case a slight shift in the frequency of some bands is observed. The results show the disappearance of some bands and the appearance of some new bands in the IR spectra when In₂O₃ is mixed in MoO₃ as well as when the mixed films are annealed in vacuum.

The structure of MoO₃ has already been discussed in detail by Anwar *et al.* [10]. The band structure of In₂O₃ which forms the natural basis of a theory of optical properties is known in detail. It has been proposed [11] that the conduction band is mainly from indium $5s$ electrons and the valence band is from oxygen $2p$ electrons. The Fermi energy E_f lies half way

between the energy bands. The structure of In₂O₃ is formed [9] by a face-centred cubic indium sublattice when three quarters of the tetrahedral vacancies between the indium atoms are occupied by the oxygen atoms; one quarter remains empty. The arrangement of these empty voids is established according to a definite pattern which is reported to repeat at intervals of 1.02 nm i.e. twice the lattice parameter of the face-centred cubic indium sublattice. This pattern can be disturbed strongly especially if the growth of the lattice occurs during the sample fabrication in vacuum by mixing In₂O₃ with some oxides by the coevaporation technique. As in In₂O₃, every fourth anion is missing [12] so the small anion sites constitute interstitial sites in the oxygen sublattice. Goswami *et al.* [13] have observed the non-stoichiometric nature of vacuum-deposited films and reported that this non-stoichiometric nature is probably due to the oxygen vacancies or metal excess. Muranaka [14] has also suggested that amorphous films deposited at room temperature have a slight excess of indium over the stoichiometric composition. Pan *et al.* [15] reported

TABLE II Infrared peak positions of amorphous 85 mol % MoO₃–15 mol % In₂O₃ thin films in the thickness range 100 to 400 nm

Sample thickness (nm)	Positions of IR bands (cm^{-1})					
	1	2	3	4	5	6
100	622 (s)	745 (sh)	845 (w)	1120 (w)	1430 (s)	1630 (s)
200	620 (s)	745 (sh)	847 (w)	1115 (w)	1440 (sh)	1630 (s)
300	620 (s)	744 (sh)	845 (w)	1115 (w)	1450 (sh)	1630 (w)
400	618 (s)	744 (sh)	843 (w)	1115 (w)	1440 (sh)	1630 (w)

TABLE III Infrared peak positions of 200 nm thick (85 mol % MoO₃–15 mol % In₂O₃) thin films in the substrate deposition temperature range 20 to 270° C

Substrate temperature (° C)	Positions of IR bands (cm^{-1})					
	1	2	3	4	5	6
20	620 (s)	745 (sh)	847 (w)	1115 (w)	1440 (s)	1630 (s)
100	615 (s)	745 (sh)	845 (w)	1100 (w)	1435 (s)	1630 (s)
200	610 (s)	744 (sh)	842 (w)	1105 (w)	1430 (s)	1630 (s)
270	611 (s)	740 (sh)	841 (w)	1104 (w)	1430 (s)	1630 (s)

TABLE IV Infrared peak positions of 200 nm thick (85 mol % MoO_3–15 mol % In_2O_3) thin films annealed in the temperature range 20 to 270°C

Annealing temperature (°C)	Positions of IR bands (cm^{-1})						
	1	2	3	4	5	6	7
200	620 (s)	745 (sh)	847 (w)	–	1115 (w)	1440 (s)	1630 (s)
200	613 (s)	743 (sh)	840 (w)	–	1107 (w)	1430 (s)	1630 (s)
300	607 (s)	739 (sh)	835 (w)	960 (w)	1104 (w)	1430 (s)	1630 (s)
400	605 (s)	735 (sh)	834 (w)	960 (sh)	1102 (w)	1430 (s)	1630 (s)
500	604 (s)	733 (sh)	833 (w)	960 (sh)	1100 (w)	1430 (s)	1630 (s)

that conduction electrons in In_2O_3 arise from the excess indium atoms. The electron concentration is proportional to the concentration of excess indium in the In_2O_3 structure.

In order to interpret the present infrared spectra of mixed films of MoO_3–In_2O_3, we first of all interpret different absorption bands in the IR spectra of pure MoO_3 and In_2O_3 films. No data on the IR spectra of pure In_2O_3 are available in the literature but different absorption bands in the spectrum of pure MoO_3 are explained below.

The absorption band at 622 cm^{-1} was attributed by Hanafi et al. [16] to the first harmonic of the fundamental frequency which is believed to have the value 307 cm^{-1}. The band at 760 cm^{-1} was attributed to the presence of Mo(VI) species. The bands at 800 and 890 cm^{-1} were attributed as being due to two different Mo–O–Mo continuous structures and pointed out that the MoO_3 contains distorted (MoO_6) octahedra in which three of the oxygen atoms are common to two octahedra and one remains unshared i.e. bonded only to the molybdenum atom. The band at 1020 cm^{-1} was attributed to the stretching vibration of independent Mo–O groups in MoO_3 oxide.

We attempt to explain the IR spectra of mixed layers of MoO_3–In_2O_3 and start by noting that the band at 554 to 576 cm^{-1} is not present in a pure MoO_3 sample but appears in the samples containing 20 mol % In_2O_3 or more. This band may be attributed to the presence of In^{3+} species. The band at 604 to 653 cm^{-1} is present in the samples containing pure MoO_3 and In_2O_3 and also in all the samples of MoO_3 with increasing In_2O_3 content, increasing substrate temperature, and increasing annealing temperature. This band is present in the pure MoO_3 samples at 622 cm^{-1}, in pure In_2O_3 at 653 cm^{-1} but it appears at 620 cm^{-1} in the sample containing 95 mol % MoO_3–5 mol % In_2O_3 and subsequently appears at lower frequencies with increasing In_2O_3 content in MoO_3. At 75 mol % MoO_3–25 mol % In_2O_3 the band appears at 612 cm^{-1}. This shift in the band towards lower frequency can be explained by assuming that when the molar percentage of In_2O_3 is increased in the mixed layers of MoO_3–In_2O_3, there is an increase of overall disorder in the system. Of the eight sites around each In^{3+} ion in the cubic In_2O_3 structure, only six are occupied by O^{2-} ions leaving two positions available

for incorporation of Mo(VI) ions. Mo(VI) ions may be incorporated in the indium interstitial positions causing a shift in the band to the lower frequency. In pure MoO_3 this band has been attributed to the first harmonic of the fundamental i.e. 307 cm^{-1}. The band at 733 to 760 cm^{-1} is present in the samples containing pure MoO_3 as well as in the mixed layers of MoO_3–In_2O_3 but is absent in pure In_2O_3 and may be attributed to the presence of Mo(VI) species [6]. The band at 833 to 861 cm^{-1} is present in all the samples with increased In_2O_3 content in the MoO_3, increased substrate temperature and increased annealing temperature. In pure MoO_3, this band appears at 800 cm^{-1} and in pure In_2O_3 this band appears at 861 cm^{-1}, but in the mixed MoO_3–In_2O_3 samples this band appears at 840 to 858 cm^{-1}. This shift in the band towards lower frequency when In_2O_3 is mixed in MoO_3 may be attributed to the incorporation of Mo(VI) ions into the indium interstitial positions. The band at 890 cm^{-1} is only present in the pure MoO_3 sample and it is absent in the mixed MoO_3–In_2O_3 samples. This band may be attributed to the Mo–O–Mo continuous structures of the MoO_3 lattice. The band at 960 cm^{-1} is only present in the samples annealed at 300°C or above and is missing in all the pure or mixed samples deposited at room temperature and at higher substrate temperatures. This band may be attributed to the formation of molybdenum species of a lower oxidation state. This new oxidation state arises from the electron transfer from oxygen $2p$ to the molybdenum $4d$ level. The band at 1020 cm^{-1} is present only in the pure MoO_3 sample. It is missing in all the samples containing In_2O_3 and may be attributed to the stretching vibration of independent Mo–O groups in the MoO_3 oxide. The band at 1100 to 1195 cm^{-1} is present in all the mixed MoO_3–In_2O_3 samples and in pure In_2O_3, but is missing in pure MoO_3. In pure In_2O_3 this band appears at 1195 cm^{-1} but in the mixed MoO_3–In_2O_3 layers it is shifted towards lower frequency and may also be attributed to the incorporation of Mo(VI) ions in the indium interstitial positions. The band at 1430 to 1550 cm^{-1} is missing in the pure MoO_3 sample but present in all mixed MoO_3–In_2O_3 samples and in pure In_2O_3. The band may be attributed to the In^{3+} oxidation state and the shift in the band frequency may also be attributed to the incorporation of Mo(VI) ions into the indium interstitial positions. The band at 1630 cm^{-1} may be caused by the presence of some lattice imperfections due to mixing the two oxides by the coevaporation technique. These results are consistent with our XPS results [9].

References

1. C. A. HOGARTH and L. A. WRIGHT, Proceedings, International Conference on Physics Semiconductors, Moscow July, (1968), (Nauka, Leningrad, 1968), p. 1274.
2. L. KIHLBORG, Arkiv Kemi 21 (1963) 471.
3. L. M. GRATTON, S. PAGLIA, F. SCATTAGLIA and M. CAVALLINI, Appl. Spectrosc 32 (1978) 310.
4. T. S. RAWAT, L. DIXIT, B. B. RAIZADA and A. K. KATIAR, Indian J. Phys 52B (1978) 193.
5. T. V. IORNS and F. ESTAFFORD, J. Amer. Chem. Soc. 88:21 (1966) 4819.
6. M. ANWAR, C. A. HOGARTH, and C. R. THEOCHARIS, J. Mater. Sci. 24 (1989) 2387.

7. B. P. KRYZHANOVSKII, *Optics and Spectrosc.* **10** (1961) 359.
8. M. ANWAR and C. A. HOGARTH, *J. Mater. Sci.* (1988), submitted for publication.
9. M. ANWAR, C. A. HOGARTH, G. A. KHAN and R. BULPETT, *Spectrochimica Acta,* submitted for publication.
10. M. ANWAR and C. A. HOGARTH, *Phys. Status. Solidi* (*a*) **109** (1988) 469.
11. J. C. C. FAN and J. B. GOODENOUGH, *J. Appl. Phys.* **48** (1977) 3524.
12. J. H. W. DE WIT, *J. Solid State Chem* **20** (1977) 143.
13. A. GOSWAMI and A. P. GOSWAMI, International Crystallographic Conference on Diffraction Studies of Real Atoms and Real Crystals, Melbourne, Australia, (Australian Acad. Sci., Canberra, 1974), 11 G.4/194.
14. S. MURANAKA, *Thin Solid Films* **151** (1987) 355.
15. C. A. PAN and T. P. MA, *J. Electrochem. Soc: Solid State Sci. Technol.* **128** (1981) 1953.
16. Z. M. HANAFI, M. A. KHILLA and A. A. SAUD *Revue de Chimie mine'rale,* **12** (1975) 546.