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The correlation of various properties of thin films of MoO_3 and of the mixed oxide systems MoO_3–In_2O_3 and MoO_3–SiO

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A discussion of the general properties of three systems of dielectric films i.e. MoO_3 and the mixed oxide systems MoO_3–In_2O_3 and MoO_3–SiO is presented. Composition, film thickness, substrate deposition temperature and annealing all have a substantial effect on the structure and various properties of the films. The general properties of these three systems of dielectric films include analysis by X-ray photoelectron spectroscopy, UV–visible and infrared spectroscopy including the Fourier transform technique, electrical properties both d.c. and a.c. at both low and high fields and electron spin resonance. An attempt is made to show how the variations of properties depend on many disposable parameters. In particular the use of X-ray photoelectron spectroscopy shows how the local atomic and molecular bonding changes as a result of varying preparation parameters and this feature is a recent facility in the field of thin dielectric–semiconducting films. It is expected that the general discussion in this paper may help in the interpretation of results on other thin dielectric and semiconducting films.

1. Introduction

In recent years considerable interest has been shown in the study of the dielectric properties of amorphous thin films due to their importance in the electronics industry. The dielectric films are extensively used as insulators and as capacitors in microelectronics. Such thin films, amorphous or crystalline, may differ in their electrical and other properties according to the manner of their preparation. We have studied many thin films of molybdenum trioxide and of the mixed oxide systems MoO_3–In_2O_3 and MoO_3–SiO prepared by a co-evaporation technique established by Hogarth and Wright [1]. Molybdenum trioxide is of interest because although it forms amorphous films when deposited onto cold substrates, it readily forms crystalline layers when the amorphous films are annealed or if films are deposited from the vapour phase on to warmed substrates. We have published a series of papers on the three systems of materials and have discussed many of their properties, electrical, optical, magnetic, structural, compositional, and so on in great detail and by using modern analytical techniques such as X-ray photoelectron spectroscopy, have been able to follow chemical bonding changes which arise from defect formation or reduction. Since we have studied this wide range of materials which include crystalline and amorphous, semiconducting and dielectric samples, it was believed to be of interest to summarise the results and to discuss, to some extent in qualitative terms, the reasons for the many interacting phenomena, not simply to analyse the results on our three series of materials, but to point to the general types of results that could be important in oxide semiconducting–dielectric layers. In other words the current essay could provide an overview of the many interacting properties which characterize this particular system and might help further in analysing other non-metallic materials in thin film form.

There is very little information available about MoO_3 because of the considerable difficulties in preparing specimens suitable for investigation for physical properties. Several researchers [2–4] have published surveys on various aspects of MoO_3. Deb and Chopoorian [3] reported that the optical absorption and ESR absorption are associated with electrons trapped by negative ion vacancies which thereby form colour centres. Ioffe *et al.* [5] have reported that electrons in the molybdenum sublattice appear as a result of oxygen deficiency for the charge compensation of impurities present in the sample and assumes that these electrons are conduction electrons. Nadkarni and Simmons [6] studied the electrical properties of MoO_3 and reported that there is a donor band between the conduction band and the valence band due to oxygen vacancies.

The study of the mixed oxide system MoO_3–In_2O_3 helps to elucidate the basic properties of these oxides. Thin amorphous dielectric films based on MoO_3 are well known as insulators but In_2O_3 is an oxide having fairly high electrical conductivity. One of the first investigations of In_2O_3 as a semiconductor was made on thin vacuum-evaporated films. Rosenberg and Lavine [7] have shown the presence of indium interstitials at remarkably high concentration. The high conduction electron concentration is believed to result from the interstitial indium atoms [8] or oxygen vacancies [9] in the In_2O_3 structure, which act as

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shallow donors. In_2O_3 is regarded as a reasonably highly conducting oxide and no information is available about its properties when deposited with MoO_3 in amorphous thin film form.

A study of various properties of evaporated thin films of the mixed oxide system MoO_3–SiO is also of considerable interest. Thin amorphous films of SiO are used extensively as optical coatings, protective layers, insulating layers for integrated circuits and also as dielectric material in thin film capacitors. It is known that vacuum-evaporated SiO films contain some dangling bonds which are structural defects and may act as trapping centres or as sources of electrons. The structure of SiO_x films has been receiving much attention in recent years and several possible structural models have been suggested. Simmons [10] reported that both donor and trapping centres are created in SiO films due to dissociation of SiO into SiO_2 and free silicon. Furthermore, the SiO structure contains active defects as a result of departures from regular structure and composition. No earlier work on mixed thin amorphous films of MoO_3–SiO is available in literature apart from recent work performed in this laboratory.

The objective of this work is to look at MoO_3 and the complex films of MoO_3–In_2O_3 and MoO_3–SiO from the point of view of modern solid state ideas particularly in terms of the structure i.e. whether crystalline or amorphous, white or blue, using modern analytical techniques. Particular attention has been given to the question of substrate temperature during deposition and also subsequent annealing, since these conditions are known to have a profound effect on the structure, composition and properties of the film. A comprehensive comparison of all the results is carried out in a correlated manner and some new ideas are presented on an established semiconducting–dielectric material.

2. Experimental work

Thin films of MoO_3, MoO_3–In_2O_3 and MoO_3–SiO were prepared by evaporation in a Balzers BA 510 coating unit on clean substrates at a pressure of 6×10^{-6} torr. The thin films of mixed oxide systems were fabricated using the co-evaporation technique established by Hogarth and Wright [1]. Molybdenum-covered boats were used for the evaporation of MoO_3 and In_2O_3 whereas tantalum-covered boats were used for the evaporation of SiO. All the other techniques used, to measure film thickness, to clean the substrates, for the preparation of thin films, for annealing the samples in vacuum, for raising the substrate temperature, and for making ESR and XPS measurements, structural investigation and film coloration processes, are the same as previously described [11]. Optical absorption measurements (ultraviolet and visible), infrared absorption measurements and electrical measurements, both d.c. and a.c. are also the same as described in the earlier work [12–15].

3. Discussion of results

A correlated study of the general properties of three systems of dielectric films, i.e. MoO_3 and mixed oxide systems MoO_3–In_2O_3 and MoO_3–SiO has included the analysis by X-ray photoelectron spectroscopy (XPS), ultraviolet and infrared spectroscopy including the use of the Fourier transform technique, electrical properties both d.c. and a.c. at both low and high fields, and electron paramagnetic resonance.

The films deposited at low temperature are amorphous in character, whereas those deposited at higher temperature and annealed at 500° C or above tend to a crystalline state. The structure of these films is studied by both electron and X-ray diffraction. The films prepared at room temperature during deposition showed no evidence of colour. As the temperature of the substrates was increased, the colour of the films changed initially to light blue and then to darker blue at higher substrate temperatures. Some samples were exposed to UV light (300 W mercury lamp) for a given period until the films turned blue. For electrical coloration the samples were fabricated in the form of a sandwich structure between evaporated metal electrodes with the substrates at room temperature during deposition, and were coloured by applying a voltage of approximately 10 V. The ESR and XPS spectra of thermally and optically coloured samples were obtained. In this broader attempt to correlate all our earlier results we have avoided including numerical examples, figues and tables but have given references to the earlier work.

3.1. MoO_3

Before discussing the observed MoO_3 results it is important to include some previous work, basic in nature, and helpful in explaining the present results.

It is well known that MoO_3 loses oxygen on heating in vacuum or in a reducing atmosphere and our amorphous layers are thus assumed to be deficient in oxygen. MoO_3 has the outer electron configuration $4s^5\,5s^1$. If MoO_3 is considered to be ionic i.e. composed only of Mo(VI) and O^{2-} ions, the valence band would be composed of oxygen 2p states and the conduction band of empty 4d and 5s states [16]. The electronic configuration of Mo(VI) is $4d^0$, so the transition from valence 2p oxygen orbitals to empty Mo(VI)$4d^0$ levels gives rise to the incorporation of lower valence Mo(V) within the lattice. Substoichiometric amorphous thin films of MoO_{3-x}, where x is a small fraction, contain a number of oxygen ion vacancies which are positively charged structural defects capable of capturing one or two electrons and into which electrons may be promoted. The oxygen vacancies occupied by two electrons act as donors. One electron may be ionized thermally while the other can only be ionized optically [17]. Thus donor centres are formed in the amorphous layers of MoO_3. These donor centres exist in the forbidden gap of the insulator and form a defect band below the conduction band [18]. In the crystalline state MoO_3 has a layer structure built up of distorted MoO_6 octahedra. The distortion is caused by the off-centre displacement of the metal atoms towards one of the surrounding oxygens. An alternative explanation of the distortion in the MoO_6 octahedra is that the crystal grows by coalescence with neighbouring crystallites as a result of the heat treatment process. When the crystallites coalesce with

neighbouring ones, MoO_6 octahedra may be combined with differently oriented MoO_6 octahedra, because the diagonal distances are similar in value. The crystals are, therefore, deformed during the growth process [11]. The oxygen distances vary from 0.188 to 0.245 nm with any particular oxygen being bound to only one Mo(VI) [19]. In evaporated MoO_3 films the predominant defects are oxygen vacancies in large concentrations [4]. The anion vacancies (V_O'') (doubly charged oxygen vacancy) capturing one or two electrons form colour centres which are similar to F and F′ centres in alkali halides. The thermal coloration of MoO_3 is probably due to the filling up of the V_O'' sites by electrons associated with the acceptor levels and also to the ionization of the V_O (uncharged oxygen vacancy) centres (whose level is close to the conduction band). This increases the concentration of V_O' (singly charged oxygen vacancy) centres. The thermal ionization of the V_O' centres is favoured by thermal annealing (in vacuum). The irradiation of the film also tends to increase the number of V_O' centres due to the capture of the released electrons by oxygen vacancies [17]. Firment *et al.* [20] studied the surface properties of stoichiometric and oxygen deficient crystalline MoO_3 by XPS, and reported that heating in vacuum induced some reduction of the MoO_3 surface and there was diffusion between the surface region and the interior of the sample.

Stoichiometric MoO_3 containing Mo(VI) has no 4d electrons, and is a diamagnetic insulator. A disturbance of its stoichiometry by the formation of oxygen vacancies causing the generation of $4d^1$ [Mo(V)] states is expected to give rise to an ESR signal [21]. Various processes have been known to produce non-stoichiometry in the oxide resulting in unpaired spins associated with the transition metal. The localization of these $4d^1$ electrons on molybdenum lattice sites can be caused by the polaron character of these charged centres. The electrical conductivity results from the transfer of d electrons from a transition metal with the lower oxidation state [Mo(V)] to an ion in a higher oxidation state [Mo(VI)] [22]. According to Stahelin and Busch [23] oxygen vacancies which capture one or two electrons act as donors in which one electron of a doubly charged centre may be ionized thermally and the other only optically. Normal ionization gives rise to two charge carriers; namely an electron and a singly charged oxygen vacancy. The number of free electrons is balanced by an equivalent number of singly charged oxygen vacancies which correspond to donors in an impurity semiconductor giving rise to electronic and ionic defect conductivity.

In the present work the optical absorption spectra of amorphous layers of MoO_3 have been studied in the thickness range 100 to 300 nm and with the substrate at room temperature during deposition. Some samples were studied in the substrate deposition temperature range 20 to 270° C and it was observed that the optical band gap decreased with the increase in both film thickness and substrate deposition temperature. Some samples were annealed in the temperature range 200 to 500° C and a decrease in the optical gap was observed with increasing annealing temperature. At about 500° C all the defects associated with a fresh film were annealed out and a crystalline state was established. Some samples were coloured optically, and some thermally, and the electrical and optical properties and the ESR and XPS spectra of these films were obtained. The films deposited on a substrate at room temperature showed no evidence of coloration. It was observed that the values of optical band gap for coloured samples were much less than for the transparent samples. ESR spectra of MoO_3 revealed that the intensity of the signal arising from Mo(V) is increased with increases in both thickness and substrate temperature. This signal vanished as a result of annealing at 300° C or above. An increase in thickness had a slight effect on the XPS core level binding energy but on heating the substrate in vacuum at 200° C or above and annealing the samples at 500° C or above, the Mo(3d) doublet appeared at lower values of binding energy. The electrical conductivity, both d.c. and a.c., is increased both with increasing thickness and with substrate deposition temperature. The electrical conductivity of the blue coloured samples is greater than that of transparent samples.

3.1.1. Effect of film thickness

The observed results are correlated as follows. The decrease in band gap with increase in film thickness is attributed to an increasing concentration of oxygen vacancies. 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 centres will effectively lower the band gap and shift the absorption edge to the longer wavelengths.

An oxygen ion vacancy with a trapped electron is probably associated with an Mo(V) ion. The increase in the ESR signal arising from Mo(V) with the increase in film thickness is due to the localization of an electron on a Mo(VI) site which gives rise to the formation of an Mo(V) site. The slight decrease in the binding energy of the Mo(3d) doublet is attributed to an increasing concentration of oxygen vacancies with increasing thickness. The band at 740 to 760 cm^{-1} in the IR study is present in the samples with increasing thickness but disappears in the samples deposited at higher substrate temperatures. This band is attributed to the increasing concentration of oxygen vacancies. The increase in conductivity, both d.c. and a.c., with increasing thickness is due to an increasing concentration of donor centres. A relatively large concentration of donor levels will help to increase the conductivity in the thicker samples.

Thus the decrease in optical band gap, the increase in the ESR signal arising from Mo(V), a decrease in the binding energy of the Mo(3d) doublet, the appearance of the absorption band at 740 to 760 cm^{-1} and the increase in conductivity with increasing thickness are all associated with an increasing concentration of oxygen vacancies when MoO_3 is thermally evaporated in vacuum.

3.1.2. Effect of substrate temperature

When the substrate temperature is increased, the

colour of the samples changes from white to blue. The reduction of the band gap in these samples is due to centres formed by capturing an electron in a doubly charged oxygen vacancy whose level lies close to the valence band. The increase in ESR signal with the increase in substrate temperature is attributed to the ionization of one electron of a doubly charged centre which gives rise to an increase in the number of singly charged oxygen centres and hence to an increase in the concentration of Mo(V) states. In the IR study the disappearance of the band at 740 to 760 cm^{-1} in the samples deposited at higher substrate temperature, is probably due to the formation of molybdenum species of lower oxidation state. On heating the substrates at 200° C or above, the Mo(3d) doublet appears at lower binding energies and indicates the formation of molybdenum species of lower valency. The binding energy of the newly formed oxidation state is in excellent agreement with the binding energy assigned to the Mo(V) oxidation state. The blue coloured films exhibit a small band near the Fermi level [24]. This band is attributed to the electrons trapped in positively charged anion vacancies within the film structure. The blue colour is caused by the interelectron transfer from an oxygen 2p to molybdenum 4d orbital that creates the isolated Mo(V) oxidation state. These results are in excellent agreement with our IR and ESR results [13, 25]. The greatly enhanced conductivity, both d.c. and a.c., of blue coloured samples is due to the higher mobility of the electrons in the defect band and the relatively small energy gap between the defect band and the conduction band.

Thus the decrease in optical band gap, the increase in ESR signal arising from Mo(V), the disappearance of the absorption band at 740 to 760 cm^{-1}, the decrease in the binding energy of Mo(3d) doublet and the increase in conductivity with the increase in substrate temperature during deposition (blue coloured samples) are all due to the interelectron transfer from oxygen 2p to molybdenum 4d orbitals that creates the isolated Mo(V) oxidation states.

3.1.3. Effect of annealing

The colour of the samples is changed to blue following annealing. The decrease in the optical band gap due to an increase in annealing temperature is in fact due to thermal ionization of electrons from doubly charged oxygen vacancies which increases the number of singly charged centres or aggregate centres and to an increase in the number of oxygen vacancies as the temperature rises. Due to increased temperature the mobility of the electrons is increased and these electrons are accumulated in certain parts of the lattice, a process which disturbs the equilibrium number of vacancies in amorphous layers. At higher annealing temperatures up to 500° C all the defects are annealed out and these aggregates are destroyed and a crystalline state is established. The ESR signal is decreased with the increase in annealing temperature and at higher annealing temperatures the ESR signal arising from Mo(V) vanishes and this is attributed to the incorporation of some oxygen ions in the lattice [25]. The oxygen is absorbed as oxygen molecules and interacts weakly with Mo(V). After annealing the samples at about 500° C the Mo(3d) doublet appears at lower binding energies and indicates the formation of molybdenum species of lower oxidation state. The creation of the Mo(V) ions in the Mo(VI) oxide lattice is the cause of the blue coloration of the samples. The increase in conductivity with increasing temperature is attributed to the higher mobility of the donors. As the concentration of oxygen vacancies increases near the negative electrode the crystal lattice becomes more regular at higher temperature with a probable influence on the mobility of the electrons.

Thus the decrease in optical band gap and the decrease in ESR signal caused by the generation of Mo(V) as a result of an increase in annealing temperature, is attributed to the decrease in dangling bond concentration when constituent atoms are connected with their neighbouring ones. The decrease in the binding energy of Mo(3d) doublet with increase in annealing temperature is due to the formation of Mo(V) species of lower oxidation state. The increase in conductivity results from increasing concentration of the oxygen vacancies near the negative electrode due to which the crystal lattice becomes more regular at higher temperatures with a probable influence on the mobility of electrons.

3.2. MoO_3–In_2O_3

The study of various properties of evaporated thin films of MoO_3–In_2O_3 prepared by the co-evaporation technique [1] helps to elucidate the basic properties of these mixed oxides. In order to interpret the observed results for MoO_3–In_2O_3 it is necessary to discuss briefly the crystallographic structure of In_2O_3. Under normal conditions In_2O_3 crystallizes in the C-type rare earth structure which is very stable [26]. The structure of In_2O_3 is body-centred cubic with eight atoms per unit cell. X-ray measurements gave a unit cell dimension of 1.01 nm. This structure is closely related to the fluorite structure but in In_2O_3 every fourth anion is missing so that small anion sites constitute interstitial sites in the oxygen sublattice. The energy of formation of oxygen interstitials in the C-type structure should be small. If the energy of migration is also small, these interstitials will be mobile and oxygen diffusion via interstitials will result, thus any primary ionic defects will be oxygen ion vacancies and indium interstitials. It has been proposed by Fan and Goodenough [16] that the conduction band in In_2O_3 arises mainly from 5s electrons and the valence band is from oxygen 2p electrons. The Fermi energy E_f in the pure material lies halfway between the energy band edges. Goswami *et al.* [27] 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. Pan *et al.* [28] reported that conduction electrons in In_2O_3 arise from the excess indium atoms. The electron conduction is proportional to the concentration of excess indium in the In_2O_3 structure.

In the present work the optical energy gap is decreased as the molar fraction of In_2O_3 is increased in In_2O_3–MoO_3 films. A decrease in band gap with increase in

film thickness, substrate temperature during deposition and annealing temperature, is observed. The ESR signal arising from Mo(V) decreases but the signal arising from In_2O_3 (some impurities in In_2O_3) increase with increase in molar fraction of In_2O_3 in In_2O_3–MoO_3. The ESR signal arising from Mo(V) vanishes on annealing in vacuum at 300° C or above. In the IR study of MoO_3–In_2O_3 the effects of changes in composition, film thickness, substrate temperature and annealing, on the absorption band positions are observed. In some cases a shift in the band frequency is also observed. Slight changes in the Mo(3d) and In(3d) peak positions are observed with the addition of In_2O_3 in MoO_3. It is noted that with both the increase in film thickness and substrate temperature during deposition, no change in the XPS spectra is observed. An appreciable change in the binding energy of the Mo(3d) and In(3d) doublets with increasing annealing temperature is observed. An increase in conductivity with increase in concentration of In_2O_3 in MoO_3 is noted. Film thickness and substrate temperature during deposition have a profound effect on the conductivity.

3.2.1. Effect of composition

The observed results are explained in the following manner. When the molar percentage of In_2O_3 is increased in the mixed layers of MoO_3–In_2O_3 there is an increase in the overall disorder in the system. The optical band gap is decreased as the concentration of In_2O_3 is increased in MoO_3. In(III) ions may be incorporated in an MoO_3 lattice causing the molybdenum orbital to be little less tightly bound. The presence of In(III) ions in an MoO_3 lattice may cause a decrease in the optical band gap. The composition has significant effect upon the area density of spins associated with the density of dangling bonds. The latter decrease linearly with increasing concentration of In_2O_3 in MoO_3. When the content of In_2O_3 is increased in the complex films, the intensity of signal arising from the Mo(V) centres is decreased, that from Mo(III) remains constant and that from impurities in In_2O_3 is increased.

Indium can exist with valencies of two and three. The valency state in which it most commonly occurs is In(III) and this state is diamagnetic and gives no ESR signal [In(III) = ns^0np^0 (no unpaired electrons)]. The new signal at $g = 1.98$ may be attributed to the presence of some impurities in In_2O_3 (the electronic configuration of indium is ns^1np^1) and not due to In(III) ions, thus the decrease in the signal arising from Mo(V) and the increase in the signal arising from the presence of impurities in In_2O_3 may be attributed to the incorporation of In(III) ions in an MoO_3 lattice which has caused the molybdenum orbital to be a little less tightly bound. In the IR study of MoO_3–In_2O_3, some new peaks appear when In_2O_3 is mixed with MoO_3. 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 containing MoO_3 with increasing In_2O_3 content, increasing substrate temperature during deposition and increasing annealing temperature. This band is present in the pure MoO_3 sample at 622 cm^{-1} in pure In_2O_3 at 653 cm^{-1} but 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, some In(III) ions are incorporated in an MoO_3 lattice, which may cause a shift in the band to lower frequency. From the XPS study of mixed oxide films of MoO_3–In_2O_3 small changes in the binding energies of the Mo(3d) and In(3d) doublets are observed with the addition of In_2O_3 to MoO_3. The binding energy of the Mo(3d) doublet is decreased slightly but there is an appreciable change in the binding energy of the In(3d) doublet. The binding energy of the pure In_2O_3 peak is 452.1 eV for $In(3d_{3/2})$ and 444.4 eV for $In(3d_{5/2})$. As In_2O_3 is added to MoO_3 the binding energy of the In(3d) doublet is increased. At 95 mol % MoO_3–5 mol % In_2O_3 the binding energy of the In(3d) doublet is 452.9 eV for $In(3d_{3/2})$ and 445.4 eV for $In(3d_{5/2})$. Conversely, as the content of In_2O_3 is increased in MoO_3 the values of the binding energy of the Mo(3d) doublet decrease. At 75 mol % MoO_3–25 mol % In_2O_3 the value for the In(3d) doublet is 452.3 eV for $In(3d_{3/2})$ and 444.9 eV for $In(3d_{5/2})$. These values are still higher than the value of the binding energy for pure In_2O_3. The position of the Mo(3d) and In(3d) lines are those expected for Mo(VI) and In(III) ions as in simple MoO_3 and In_2O_3 respectively. This effect can be explained by assuming that the incorporation of In(III) ions in an MoO_3 lattice has led to overall disorder in the mixed layers of MoO_3–In_2O_3. The presence of In(III) ions in an MoO_3 lattice has caused the molybdenum orbital to be a little less tightly bound and this has decreased the binding energy of the Mo(3d) and In(3d) doublets. The electrical conductivity, both d.c. and a.c., is increased when the content of In_2O_3 is increased in MoO_3. This increase in d.c. conductivity with composition 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, In(III) ions may be incorporated in an MoO_3 lattice leading to an increased free electron concentration. The increase in the a.c. conductivity may be attributed to defects in the MoO_3–In_2O_3 films caused by decomposition during the evaporation process and by the movement of the dipoles under the influence of an external field. The incorporation of In(III) ions in an MoO_3 lattice may also enhance the a.c. electrical conductivity.

Thus the decrease in optical band gap, the decrease in the ESR signal arising from Mo(V) and increase in the ESR signal arising from the impurities in In_2O_3, the shift in the IR band frequency from 620 to 653 cm^{-1}, the decrease in the binding energies of Mo(3d) and In(3d) doublets and the increase in the electrical conductivity, both d.c. and a.c., with increase in concentration of In_2O_3 in MoO_3, may be due to the incorporation of In(III) ions in an MoO_3 lattice.

3.2.2. Effect of film thickness

The optical band gap decreased with increase in film

thickness of the samples having fixed composition 85 mol % MoO_3–15 mol % In_2O_3. When the thickness of the samples is increased, the concentration of oxygen vacancies i.e. positively charged structural defects, is increased in both MoO_3 and In_2O_3. The incorporation of In(III) ions in an MoO_3 lattice may also enhance the electron concentration but the oxygen vacancies are believed to be the source of conduction electron states in the MoO_3–In_2O_3 complex. The intensity of the signal arising from Mo(V) is increased but the intensity of the signal arising from impurities in In_2O_3 and Mo(III) remains constant with the increase in thickness of the samples. This increase in the spin density of the signal arising from Mo(V) with the increase in thickness of the samples can be explained by assuming that amorphous layers of MoO_3 contain a number of oxygen vacancies which are positively charged structural defects capable of capturing one or two electrons. The oxygen vacancies in capturing one or two electrons, give rise to singly charged centres, and an oxygen ion vacancy with trapped electrons is probably associated with an Mo(V) ion. Localization of an electron on an Mo(VI) site gives rise to the formation of an Mo(V) site and hence to an increase in the ESR signal. The IR study of MoO_3–In_2O_3 films reveals that there is no effect of film thickness on the IR absorption band frequencies. There is no evidence for appearance of new bands or the disappearance of any band with increasing thickness of the samples having fixed composition (85 mol % MoO_3–15 mol % In_2O_3). Measurements of the XPS core level spectra of MoO_3 with increasing thickness reveal that the values of binding energy of the Mo(3d) and In(3d) doublets are almost constant. An increase in conductivity (both d.c. and a.c.) is observed with increasing thickness of the samples having composition 85 mol % MoO_3–15 mol % In_2O_3. Oxygen vacancies in oxide compounds have been reported by Aleshin *et al.* [29], Goswami *et al.* [27] and Dzhanelidze *et al.* [17]. When MoO_3 and In_2O_3 are heated in vacuum during evaporation, oxygen vacancies are created with increasing thickness (in both oxides). The oxygen deficiency in MoO_3–In_2O_3 films results in the formation of dipoles which contribute to the a.c. conductivity. The incorporation of In(III) ions in an MoO_3 lattice may also enhance the electron concentration but the higher mobility of ionic defects is caused by the oxygen vacancies which are believed to be the source of conduction electrons in the MoO_3–In_2O_3 complex. Higher impurity concentration means that the dielectric layer would show considerable conductivity at room temperature.

The decrease in optical band gap, the increase in the ESR signal arising from Mo(V) and the increase in conductivity (in the mixed MoO_3–In_2O_3 samples having fixed composition 85 mol % MoO_3–15 mol % In_2O_3) with increasing thickness, are all attributed to the increasing concentration of oxygen vacancies in the MoO_3 and In_2O_3 lattice.

3.2.3. Effect of substrate temperature
The optical band gap is decreased with the increase in substrate deposition temperature in the mixed oxide films of constant thickness and fixed composition (85 mol % MoO_3–15 mol % In_2O_3 having thickness $\approx$ 300 nm). Rosenberg [30] has suggested the movement of In_i (indium interstitial) defects while measuring the oxidation state of indium metal at higher substrate temperatures. The decrease in optical band gap with increasing substrate temperature may be due to the increasing concentration of these types of defects and the formation of molybdenum species of lower oxidation state. There is a very small effect of substrate deposition temperature on the ESR signal of mixed MoO_3–In_2O_3 samples. There is no shift observed in the Mo(3d) and In(3d) line positions when the substrates are heated in vacuum during deposition in the range 20 to 270° C. Very slight changes are observed in the band frequencies of the samples with increasing substrate temperature. The conductivity of MoO_3–In_2O_3 samples is increased with the increase in substrate temperature during deposition. In MoO_3 a number of oxygen vacancies are created during the evaporation process and these oxygen vacancies may be ionized thermally and give rise to two charge carriers, an electron and a singly charged oxygen. In In_2O_3 two kinds of ionic defects can occur as donors at higher temperatures, namely oxygen vacancies and indium interstitials. Both types of defects contribute to the conductivity. The increase in conductivity with increase in substrate temperature is ascribed to the increasing concentration and higher mobility of these types of donors.

The decrease in optical band gap and increase in conductivity with the increase in substrate temperature may thus be due to the increasing concentration of oxygen vacancies and indium interstitials.

3.2.4. Effect of annealing
The decrease in the optical band gap of 85 mol % MoO_3–15 mol % In_2O_3 samples of thickness $\approx$ 300 nm due to the increase in annealing temperature may result from a reduction in the concentration of lattice imperfections due to annealing the substrate in vacuum. At higher annealing temperature, up to 500° C, most of the defects are annealed out and a crystalline state is established. The ESR signals arising from Mo(V) centres vanish and those from impurities in In_2O_3 decrease when the samples are annealed in vacuum for two hours at 500° C at a pressure of 10^{-3} torr. Oxygen is assumed to be incorporated in the MoO_3 lattice, which has caused the Mo(V) signal at $g = 1.92$ to vanish. The oxygen is absorbed as oxygen molecules and these interact with the paramagnetic species. Therefore Mo(V) will disappear by electron transfer from one Mo(V) to another Mo(V) site, because of the increase in the instability of Mo(V) states induced by absorption of oxygen. The Mo(V) signal disappears in accordance with the scheme proposed by Sotani [31]. The decrease in the ESR signal arising from impurities in In_2O_3 may be due to the oxygen vacancies and indium interstitials produced in In_2O_3 at higher temperatures. The IR studies of MoO_3–In_2O_3 films reveal that 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 lower oxidation state. The binding energy of the Mo(3d) and In(3d) doublet is decreased with the rise in annealing temperature. A plausible explanation of the annealing effect on binding energies arises as a result of two kinds of ionic defects which are produced in In_2O_3 at higher temperatures namely, oxygen vacancies and indium interstitials. The decrease in binding energy of the In(3d) doublet may be due either to the increasing concentration of these types of defects or to the formation of indium ions of lower oxidation state. The decrease in binding energy of the Mo(3d) doublet may be due to the formation of molybdenum species of lower oxidation state so that an Mo(VI) centre may be changed to Mo(V). By annealing the samples at 500° C the formation of Mo(IV) valency states [32, 33] may be expected. The increase in conductivity in mixed oxide films (85 mol % MoO_3–15 mol % In_2O_3 having thickness ≈ 300 nm) due to increase in temperature is ascribed to the increasing concentration of electrons and singly charged oxygen vacancies (oxygen vacancies capable of capturing one or two electrons may be ionized thermally). Normal ionization gives rise to two charge carriers, an electron and a singly charged vacancy, in MoO_3 and oxygen vacancies and indium interstitials in In_2O_3.

Thus the decrease in optical band gap, the decrease in ESR signal arising from Mo(V) and impurities in In_2O_3, the appearance of the band at $960\,cm^{-1}$, the decrease in the binding energies of the Mo(3d) and the In(3d) doublets and the increase in conductivity are attributed to the formation of molybdenum species of lower oxidation state and increasing concentration of oxygen vacancies and indium interstitials.

3.3. MoO_3–SiO

The most fundamental information needed to understand the various properties of MoO_3–SiO amorphous films is the structural arrangements of the constituent atoms in these materials. The silicon oxide structure contains active defects, as it departs from the structure and composition which is taken as ideal, i.e. that of amorphous SiO_2. These defects are associated with oxygen deficiencies in the film giving rise to vacancy states and unstable structural defects i.e. interstitial oxygen [34]. Thin films of SiO are often prepared by heating the commercial SiO powder in vacuum. The resulting SiO film may be structurally quite different from the SiO starting material. Silicon and oxygen may combine to form amorphous materials of composition SiO_x where x may vary from 1 to 2. SiO is by no means a simple mixture of silicon and SiO_2. Several structures different from those associated with simple silicon and SiO_2 are present. As SiO_x can exist in all intermediate compositions between Si and SiO_2, the possible chemical bonds i.e. Si–Si and Si–O, are distributed in a statistical manner. Philipp [35] concluded that optical phenomena could be qualitatively accounted for by the presence of groups of Si–O and Si–Si bonds. The theory of atomic arrangements in these solids as proposed by Temkin [36] and which is taken to apply at all values of x is based on the following assumptions. (i) Each silicon atom is bound to four other atoms. (ii) Each oxygen atom is bound to two other atoms. (iii) Oxygen atoms do not bond with each other. (iv) The average Si–Si bond length is 0.235 nm. (v) The average Si–O bond length is 0.162 nm. The structure of SiO_x films is generally described within the framework of one of the two models, the mixture model and the random bonding model. According to the mixture model the particles of silicon and quartz which make up this material contain Si–(Si_4) and Si–(O_4) tetrahedra only, with equal proportions. According to the random bonding model SiO cannot be considered to be a simple mixture of silicon and quartz. The non-stoichiometric SiO_x films are a statistical mixture of five randomly bonded tetrahedra Si–(Si_yO_{y-4}) i.e. a complete mixture of Si–Si and Si–O bonds on an atomic scale, with a possibility of y being 0, 1, 2, 3, and 4 with the Si–(Si_3O), Si–(Si_2O_2) and Si–(SiO_3) arrangements being more likely. Thomas *et al.* [37] have related the spins to the internal surfaces of voids. By voids they mean defects larger than atomic size (di-, tri-, tetra-, penta-vacancies are examples of atomic size defects), and the spin density is proportional to the surface area of the voids. Dangling bonds are present in the amorphous SiO films due to the presence of voids and according to Brodsky *et al.* [38] every second crystallite has dangling bonds. Timson *et al.* [39] reported that the ESR originates in SiO from the unpaired electrons of silicon atoms due to broken bonds. Brower *et al.* [40] and Paez *et al.* [41] reported that unpaired electrons are localized on the oxygen atoms rather than on silicon, thus in the case of SiO it is believed that unsaturated bonds of oxygen atoms give rise to ESR signals. Nelson and Weeks [34], have reported that vacuum evaporation may lead to the incorporation of defect centres consisting of an oxygen ion vacancy with trapped electrons in SiO films. The behaviour of these defect centres appears to be analogous to that of F and F′ centres in alkali halides. They also reported that thermal release of the trapped electrons was possible. Another centre i.e. an interstitial non-bridging oxygen ion, was a very common defect in silicon glasses. In SiO the valence band consists of silicon 3s and 3p orbitals and the conduction band consists of the oxygen 2p orbital. An evaporated insulating SiO film is an imperfect structure and must contain a high trap density, the effect of which is to reduce the conductivity of the film. According to Simmons [10] donor centres are created in SiO films due to the dissociation of SiO into SiO_2 and free silicon.

In this work the optical band gap decreased as the molar percentage of SiO was increased in MoO_3–SiO films. A decrease in the band gap with increase in film thickness, substrate deposition temperature and annealing is observed. At higher annealing temperatures (400 to 500° C) the optical band gap starts to increase. The ESR signal arising from Mo(V) decreases and that of defect states in SiO increases as the content of SiO is increased in MoO_3. Both the signals (arising from Mo(V) and defect states in SiO) are increased

with the increase in film thickness of 70 mol % MoO_3–30 mol % SiO samples. The ESR signal arising from Mo(V) increases while the signal arising from defect states in SiO decreases with the rise of substrate temperature. The ESR signal arising from Mo(V) first increases and then decreases while the signal arising from the defect states in SiO first decreases and then increases with the rise of annealing temperature. When SiO is mixed in MoO_3 some new bands appear. A slight shift in the frequencies of certain bands is observed. Film thickness, substrate deposition temperature and annealing have no profound effect on the IR absorption bands. In the XPS study of MoO_3–SiO thin films, appreciable changes in the Mo(3d) doublet and Si(2p) line positions are observed when the concentration of SiO is increased in MoO_3. Film thickness has a very slight effect but substrate temperature during deposition and annealing has a profound effect on the core level binding energies of Mo(3d) and Si(2p). Conductivity both d.c. and a.c., is decreased when the content of SiO is increased in MoO_3. An increase in conductivity with the rise in temperature is observed in the MoO_3–SiO films of fixed composition.

3.3.1. Effect of composition

The optical band gap is decreased as the content of SiO is increased in MoO_3 and this result supports the idea that in MoO_3–SiO films, indirect transitions occur with much stronger absorption because the **k** vector is not uniquely defined in the disordered material. In amorphous SiO there exists a large density of localized states in the forbidden gap which can be considered as trapping and/or donor-like states [10]. The donor centres formed in the amorphous layers of MoO_3 exist in the forbidden gap of the insulator [12]. Thus the decrease in optical gap with the addition of SiO in MoO_3 is attributed to the increase in disorder and the presence of defects (oxygen-ion vacancies, dangling bonds at point defects, microvoids, interstitial non-bridging oxygen ions, donor and trap centres etc.) in the MoO_3–SiO complex structure. When the molar percentage of SiO is increased in MoO_3, the ESR signal arising from Mo(V) is decreased but the signal arising from defect states in SiO is increased. This effect can be explained by assuming that spins are associated with the internal surfaces of voids due to the open structure. The increase in the content of SiO in MoO_3 may enhance the density of dangling bond centres in the MoO_3–SiO complex and hence the ESR signal attributed to defect states in SiO is increased. Some local bonding between the MoO_3 and SiO components of the thin film may slightly reduce the signal attributed to Mo(V). An IR study of MoO_3–SiO reveals that the band at 940 cm^{-1} is present in all the samples containing SiO but not in the sample containing pure MoO_3. This band may be attributed to the absorption of oxygen atoms in its twofold coordination bridging Si–O–Si bond at an isolated site. This means that there is no oxygen atom as a second-nearest neighbour to any other oxygen atoms, and this result is consistent with those of the other workers [36, 42]. Appreciable changes in the binding energy of the Mo(3d) and Si(2p) line positions are observed with varying composition. The value of the core level binding energy of the Mo(3d) doublet is decreased while the value of core level binding energy of the Si(2p) lines is increased. The value of the binding energy of a pure SiO film is 101.8 eV but when SiO is mixed in MoO_3 the value of binding energy is increased to 102.0 eV at 90 mol % MoO_3–10 mol % SiO and thereafter increases slowly with the increase in concentration of SiO in MoO_3. These results can be explained by assuming that some silicon ions may be incorporated in an MoO_3 lattice and may cause the molybdenum orbital to be a little less tightly bound, as a result of which the binding energy of the Mo(3d) doublet may decrease. In the amorphous Si : O system, the oxygen atom is more electronegative than silicon, so that the direction of charge transfer in the Si–O bond is expected to be from the silicon atom to the oxygen atom. The effect of this charge transfer is to increase the binding energy of a Si(2p) core state relative to its value in elemental Si(2p) [42, 43]. During the SiO evaporation, some SiO is dissociated and deposited as non-oxidizing silicon atoms and oxygen atoms. The oxygen atoms presumably oxidize the partially oxidized silicon atoms. This will also result in a small increase in the Si(2p) binding energy [44]. The change in SiO composition (in SiO_x the value of x may change typically from 1 to 2) may also cause the binding energy of the Si(2p) lines to increase as the content of SiO is increased in MoO_3. SiO is a better insulator than MoO_3 due to its wider band gap. When the content of SiO is increased in MoO_3, the conductivity is decreased. This result can be explained by assuming that during evaporation the silicon ions incorporated in the MoO_3 lattice increase the overall disorder in the system. When the content of SiO is increased in MoO_3 the incorporation of trapping centres is increased in the mixed MoO_3–SiO films due to the imperfect structure of evaporated SiO, as a result of which the conductivity of the mixed MoO_3–SiO films is decreased.

Thus the decrease in the optical band gap, the decrease in the ESR signal arising from Mo(V) and the increase in the ESR signal arising from the defect states in SiO, the appearance of the band at 940 cm^{-1} in the IR study, the decrease in the binding energy of the Mo(3d) doublet and increase in the binding energy of Si(2p) lines when the content of SiO is increased in MoO_3, may be due either to the incorporation of silicon ions in an MoO_3 lattice or to the change in SiO composition. The decrease in conductivity with increasing concentration of SiO in MoO_3 may be attributed to the increasing number of trapping centres generated in MoO_3–SiO films during the evaporation process.

3.3.2. Effect of thickness

The optical band gap decreased with the increase in thickness of the samples (70 mol % MoO_3–30 mol % SiO) and this may be explained by assuming that the concentration of oxygen vacancies i.e. positively charged structural defects is increased in both MoO_3 and SiO. 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 centres will effectively lower the band gap and shift the absorption to the longer wavelengths. ESR signals arising from Mo(V) and defect state densities in SiO increase with the increase in thickness of the samples. Dangling bonds in SiO are likely to be created during the deposition process. When the thickness of the samples is increased, an amorphous network with a more open structure is built up, thus increasing to some extent the dangling bond density which thus causes the ESR signal associated with them to increase. In amorphous MoO_3, oxygen vacancies are created and these oxygen vacancies with trapped electrons are associated with Mo(V) ions [25]. Thus the increase in ESR signal arising from Mo(V) is due to the increasing concentration of Mo(V) sites when the thickness of the samples is increased. The thickness has only a very slight effect on the IR band frequencies and no new band appears with increase in thickness of the samples. Measurements of core level spectra of MoO_3–SiO samples with increasing thickness reveal that the values of the binding energy are almost constant with increasing thickness.

The decrease in the optical band gap and the increase in the ESR signals (arising from both Mo(V) and defect states in SiO) with increasing thickness of the samples, are thus attributed to the increasing concentration of oxygen vacancies, dangling bonds and Mo(V) sites.

3.3.3. Effect of substrate temperature

When the substrate temperature during deposition is increased, the optical band gap is decreased in the samples of 70 mol % MoO_3–30 mol % SiO having thickness 300 nm. It has been suggested that the substrate temperature influences the composition of the films of vacuum-evaporated SiO. In particular the silicon–oxygen bond dissociates if the films are deposited on substrates heated at 400° C or above. The study of the MoO_3 films at higher substrate temperatures has revealed the formation of molybdenum species of lower oxidation state [Mo(V)] [45]. The decrease in the optical band gap due to increase in the substrate temperature is due to the release of trapped electrons by thermal energy or the outward diffusion of oxygen-ion vacancies which are quite mobile even at the lower temperatures. As the substrate temperature is increased, less interstitial oxygen and more oxygen vacancies are incorporated in the oxide and this together with the formation of molybdenum species of lower oxidation state is the main cause of the reduction of the optical band gap in these mixed films of MoO_3–SiO. The substrate deposition temperature has a considerable affect on the intensity of the ESR signal of mixed MoO_3–SiO films. The ESR signal attributed to dangling bonds ($g = 2.004$) is decreased while the signal arising from Mo(V) is increased with the increase in substrate temperature. The decrease in ESR signal arising from the defect states in SiO is due to the removal of voids which causes a decrease in the number of dangling bonds. The increase in the ESR signal arising from Mo(V) may be due to an increase in the concentration of Mo(V) states as the substrate temperature is raised [25]. The substrate temperature has no effect on the IR absorption bands but a considerable effect on the binding energy of the Mo(3d) doublet and a slight effect on the binding energy of Si(2p) lines is observed. Heating the substrate in vacuum at 200° C or above causes the Mo(3d) doublet to appear at lower binding energies and indicates the formation of molybdenum species of lower oxidation state. The binding energy of the newly formed molybdenum oxidation state is in excellent agreement with the binding energy assigned to the Mo(V) oxidation state [45, 46]. This decrease in the binding energy of the Mo(3d) doublet may be due to electron transfer from an oxygen (2p) to a Mo(4d) level. The slight change in the binding energy of Si(2p) lines with the increase in substrate temperature may be due to dissociation of SiO to silicon and oxygen atoms resulting in the small increase in Si(2p) binding energy. Heating the substrate does not alter the O : Si ratio but does lead to internal chemical changes in the film [44].

The decrease in the optical band gap, the increase in the ESR signal arising from Mo(V), the decrease in the signal arising from the defect states in SiO and the decrease in the binding energy of the Mo(3d) doublet and the increase in the binding energy of Si(2p) lines are thus due to the removal of voids, the dissociation of SiO to silicon and oxygen atoms and to the formation of molybdenum species of lower oxidation state.

3.3.4. Effect of annealing

The optical band gap is decreased with the increase in annealing temperature in the lower temperature ranges but at 400 to 500° C the optical band gap is increased. The decrease in the optical band gap with the increase in annealing temperature up to 300° C arises from the fact that thermal disorder in the samples is increased and consequently the band tailing starts at lower energies. The increase in the band gap at 400° C or above may be due to the removal of voids and to a decrease in the number of unsaturated bonds. Moreover the films relax to a lower free energy configuration, the volume densities of the gaseous impurities and dangling bonds fall, and the bond lengths and angles redistribute themselves. This in turn reduces the localized level concentration and consequently the optical band gap is increased. Annealing has a significant affect in reducing the spin density and this is attributed to a rearrangement of the atoms and to the removal of voids thereby causing a decrease in the number of unsaturated bonds with the increase in annealing temperature up to 300° C. Moreover oxygen is initially absorbed as oxygen molecules and these interact with the paramagnetic species causing a decrease in the ESR signal with increasing annealing temperature. A slight increase in the ESR signal arising from Mo(V) when the sample is annealed at 200° C, may be due to an increase in the density of Mo(V) states due to heating. This signal is diminished at higher annealing temperatures due to incorporation of oxygen in the matrix. The ESR signal associated with the dangling bonds in SiO starts increasing when the samples are annealed at 400° C or above, an observation which may be attributed to the production of such dangling bonds around the crystallites in the

process of crystallization. The production of such dangling bonds with annealing has also been suggested by Hasegawa *et al.* [47]. The binding energy of the Mo(3d) doublet is decreased but that of the Si(2p) lines is increased as the annealing temperature is increased. After annealing the samples at 500° C the Mo(3d) doublet appears at lower binding energies and indicates the formation of Mo species of lower oxidation state. The binding energy of the Mo(3d) doublet is in excellent agreement with the binding energy assigned to the Mo(V) oxidation state [32, 33]. The affect of annealing on the binding energy of Si(2p) lines is not very pronounced. The value of binding energy of Si(2p) lines of the samples with increasing annealing temperature is the same for the samples whose substrate was heated to 270° C during deposition and an explanation similar to that proposed for the samples deposited at higher substrate temperature probably applies. The decrease in the binding energy of the Mo(3d) doublet at higher annealing temperature can be explained by assuming that some silicon ions may be incorporated in an MoO_3 lattice which has caused the Mo orbital to be a little less tightly bound. This helps the electron transfer from an oxygen (2p) to a molybdenum (4d) level due to which the molybdenum is readily changed to a lower oxidation state during heat treatment. The conductivity in MoO_3–SiO films of fixed composition is increased with the increase in temperature and this result can be explained by assuming that vacuum evaporation leads to the incorporation of defect centres consisting of an oxygen ion vacancy with trapping electrons in SiO films. MoO_3 films also contain a number of oxygen vacancies capable of capturing one or two electrons. These oxygen vacancies are analogous to F and F′ centres in alkali halide crystals and act as donors. The increase in conductivity due to increase in temperature is due to an increasing concentration of donors. Increased mobility of donors and thermal release of trapped electrons may also enhance the conductivity at higher temperature.

The decrease in the optical band gap, the decrease in ESR signal arising from both Mo(V) and defect states in SiO, the decrease in binding energy of the Mo(3d) doublet and the increase in the binding energy of Si(2p) lines with increase in annealing temperature, may thus be due either to the interelectron transfer from an oxygen (2p) to a Mo 4d level as a result of which, molybdenum is readily changed to a lower oxidation state during heat treatment, or to the removal of voids and a decrease in the number of unsatisfied bonds. A slight increase in the optical band gap and ESR signal arising from defect states in SiO at 400° C or above may be due to the dangling bonds in the amorphous regions surrounding crystallites newly produced during the annealing process. The increase in conductivity of MoO_3–SiO films with increase in temperature is attributed to the increasing concentration and higher mobility of donors.

4. Conclusion

It is thus concluded that changes in the optical, ESR, IR, XPS and electrical properties of MoO_3 films with the increase in film thickness are all ascribed to the increasing concentration of oxygen vacancies which are incorporated in the film structure during vacuum evaporation. The changes with increase in substrate temperature during deposition are due to the formation of molybdenum species of lower oxidation state which are formed from the electron transfer from the oxygen 2p to the molybdenum 4d level. The changes with increase in annealing temperature are due either to the formation of molybdenum species of lower oxidation state or to a decrease in the concentration of dangling bonds. When In_2O_3 is incorporated in MoO_3, some In(III) ions are introduced into an MoO_3 lattice and this causes the molybdenum orbital to be a little less tightly bound. As a consequence, the optical, ESR, IR, XPS and electrical properties of the mixed oxide system (MoO_3–In_2O_3) are changed. The changes associated within the mixed oxide system MoO_3–In_2O_3 with increase in thickness are due to an increase in the concentration of oxygen vacancies in MoO_3 and In_2O_3, and those resulting from an increase in substrate temperature are due to an increasing concentration of oxygen vacancies and indium interstitials. The changes associated in the mixed oxide system MoO_3–In_2O_3 with an increase in annealing temperature are due to the formation of molybdenum species of lower oxidation state and to an increasing concentration of oxygen vacancies and indium interstitials. The changes ascribed to the mixed oxide system MoO_3–SiO with the increase in composition may be due either to the incorporation of silicon ions in an MoO_3 lattice or to the change in SiO_x composition. Those related to an increase in film thickness are due to increasing concentrations of oxygen vacancies. Mo(V) sites and dangling bonds. The changes in various properties of the mixed oxide system MoO_3–SiO related to the increase in substrate temperature are due to the removal of voids, the dissociation of SiO into silicon and oxygen atoms and the formation of molybdenum species of lower oxidation state. Those related to the increase in annealing temperature are due to the incorporation of silicon ions in an MoO_3 lattice or to the removal of voids and a decrease in dangling bond concentration. A slight increase in the optical band gap and ESR signal arising from defect states in SiO at 400° C or above may be due to the dangling bonds in the amorphous regions surrounding crystallites newly produced during the process of annealing. The increase in conductivity with increase in temperature is due to the increasing concentration and higher mobility of donors.

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