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An XPS study of amorphous MoO_3/SiO films deposited by co-evaporation

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X-ray photoelectron spectroscopic (XPS) core-level spectra of MoO_3/SiO thin films are presented. The effects of changes in composition, substrate temperature during deposition and annealing on the binding energy of Mo(3d) and Si(2p) core lines in mixed films are compared with those of MoO_3 and SiO. Appreciable changes in Mo(3d) peak positions and slight changes in Si(2p) peak positions are observed. The change in binding energy of the Mo(3d) doublet may be attributed to the effective incorporation of silicon ions in an MoO_3 lattice which may cause the molybdenum orbital to be a little less tightly bound. This helps in the internal electron transfer from the oxygen (2p) to the molybdenum (4d) level as a result of which the molybdenum is readily changed to lower oxidation states during heat treatment. XPS spectra show that the position of the Si(2p) core state shifts monotonically with increasing oxygen concentration from the value of 101.8 to 102.6 eV.

1. Introduction

One of the powerful modern physical methods for the investigation of electronic structure of materials is X-ray photoelectron spectroscopy (XPS). This technique is being used today in many laboratories for a wide range of applications (e.g. investigation of band structure of crystals, the binding state of atoms in chemical compounds, surface chemistry and structural analysis of chemical substances). Because of the low penetration depth (λ) the method is very well suited for the investigation of thin layers. In this study we report the preparation of MoO_3/SiO mixed thin films to elucidate the electronic structure of these mixed oxides. Photoelectron studies of core levels of these materials are therefore of great interest. The need for such studies is further increased by the fact that relative band calculations are currently not available for these oxides because of their complex structure. Experimental analytical studies are therefore required to assess the value of the theoretical approach to the electronic structure of these materials.

MoO_3 is an insulator which has an unusual layer structure and exhibits several interesting physical properties. Substoichiometric molybdenum trioxide offers possibilities for superionic conduction [1]. Rabalais *et al.* [2] reported that the band in the region of the 4d states is caused by the trapping of electrons in oxygen vacancies. These defects imply a deviation (MoO_{3-x}) from exact stoichiometric composition (MoO_3) and give rise to a defect band which causes the electrical conductivity to increase.

There is also considerable interest in the atomic structure of the suboxides of silicon. Extensive investigations of electronic properties of amorphous silicon oxide layers show that their stoichiometry is strongly influenced by the preparation conditions. Films deposited at low substrate temperature are single phase, but annealing at higher temperature may promote a phase separation into SiO_2 and Si [3]. Philipp [3] proposed a model from optical data for chemical bonds in SiO but little firm information on the structure of these layers is available.

We have studied the effects of substrate temperature during deposition, etching and annealing on the structural properties of MoO_3 thin films by XPS [4, 5] and reported that MoO_3 turned blue when the substrate temperature during deposition was raised above 373 K. XPS spectra supported the formation of the Mo(V) oxidation state in the blue samples. Both etching and annealing changed the MoO_3 surface to a lower oxidation state. In another investigation [6] we have studied the mixed MoO_3/In_2O_3 thin films fabricated by the co-evaporation technique and reported that some In(III) ions were incorporated in an MoO_3 lattice which caused the molybdenum orbital to be a little less tightly bound and resulted in a decrease of binding energy of the Mo(3d) and In(3d) doublets as the relative content of In_2O_3 was increased in MoO_3. We have also studied MoO_3/SiO thin films by electron spin resonance (ESR) [7] and by infrared [8] measurements and reported that an increase in the ESR signal at $g = 2.004$ by annealing the samples at 400° C or above is due to the dangling bonds in amorphous regions surrounding the crystallites newly produced during the annealing process. The band at 940 cm^{-1} was attributed to the absorption of oxygen atoms by the two-fold coordinated bridging Si–O–Si bond at an isolated site, indicating that there is no oxygen atom as a second nearest neighbour to any other oxygen atom [8]. The objective of the present investigation is to study the XPS core level measurements so as to analyse the changes in chemical nature and electronic

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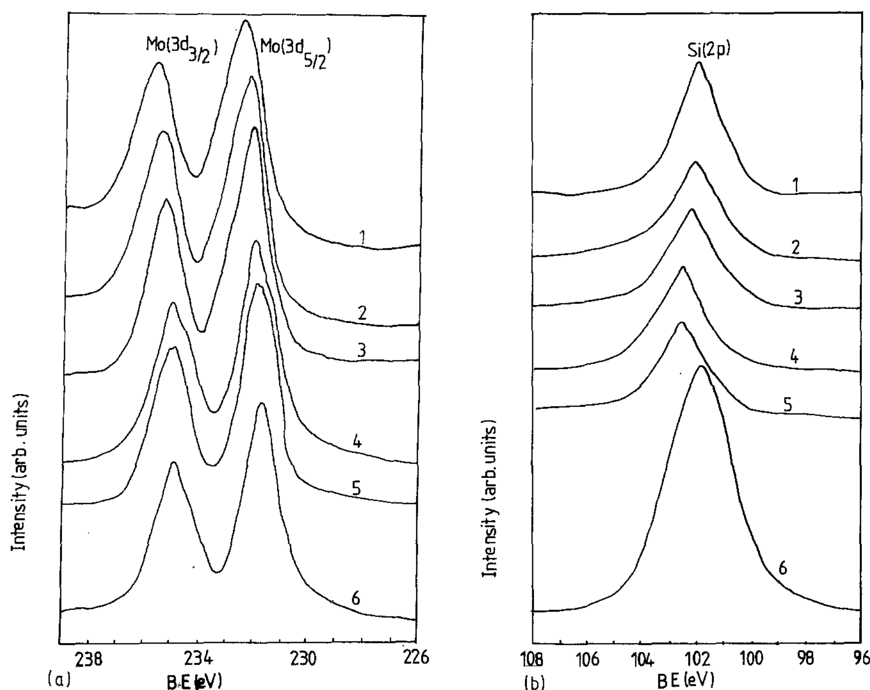

Figure 1 (a) XPS core-level Mo(3d) spectra of MoO_3 for 300 nm thick samples of varying composition (mol %) with the substrates at room temperature during deposition: (1) 100 MoO_3, (2) 90 MoO_3/10 SiO, (3) 80 MoO_3/20 SiO, (4) 70 MoO_3/30 SiO, (5) 60 MoO_3/40 SiO, (6) 50 MoO_3/50 SiO. BE = binding energy. (b) XPS core-level Si(2p) spectra of SiO for 300 nm thick samples of varying composition (mol %) with the substrates at room temperature during deposition: (1) 90 MoO_3/10 SiO, (2) 80 MoO_3/20 SiO, (3) 70 MoO_3/30 SiO, (4) 60 MoO_3/40 SiO, (5) 50 MoO_3/50 SiO, (6) 100 SiO. BE = binding energy.

structure of thin amorphous MoO_3/SiO films at different compositions, substrate deposition temperatures and annealing temperatures.

2. Experimental work

Thin evaporated layers of MoO_3/SiO were deposited on clean Corning 7059 glass substrates held at a pressure of about 6×10^{-6} torr in a Balzers BA 510 coating unit. Molybdenum and tantalum boats were used for the evaporation of MoO_3 and SiO, respectively. All other techniques used to measure the film thickness, cleaning of the substrates, annealing the samples and XPS measurements are the same as described in earlier work [4]. The binding energy scale was calibrated by assigning a value of 284.6 eV to the C(1s) signal as suggested by Wagner *et al.* [9].

3. Results

The XPS core-level spectra of MoO_3/SiO mixed thin films have been studied for samples of constant thickness ($\approx$ 300 nm) but of different compositions. Some samples of 300 nm thickness were studied at various substrate temperatures during deposition in the range 20 to 270° C. A few samples were annealed in vacuum for 2 h in the range 200 to 500° C. Figs 1a and b show the XPS core-level Mo(3d) and Si(2p) spectra of MoO_3 and SiO, respectively, for 300 nm thick samples of varying compositions. The position of the Mo(3d) doublet is shifted towards the lower binding energies but the position of the Si(2p) lines is shifted towards higher binding energies as the content of SiO is increased in MoO_3. Figs 2a and b show the XPS core-level Mo(3d) and Si(2p) spectra of MoO_3 and SiO for a 300 nm thick 70 mol % MoO_3/30 mol % SiO sample at four different substrate temperatures during deposition in the range 20 to 270° C. Slight shifts in both Si(2p) and Mo(3d) line positions are observed with the rise of substrate temperature. Figs 3a and b show the XPS core-level Mo(3d) and Si(2p) spectra of MoO_3 and SiO, respectively, of 300 nm thick 70 mol % MoO_3/30 mol % SiO deposited at room temperature and annealed in the temperature range 200 to 500° C. When the samples are annealed in vacuum for 2 h, there is an appreciable shift in the position of the Mo(3d) doublet towards lower binding energies. After annealing the samples at 500° C the shift in the Mo(3d) line position is in close agreement with the line position of Mo(IV) [10, 11]. In Figs 2a and b and 3a and b the top line provides the reference point obtained from untreated samples with the substrates at room temperature during deposition. Tables I to III show the photoelectron binding energies of Mo(3d) and Si(2p) core electrons in terms of composition, increasing substrate temperature and annealing temperature, respectively. Table IV shows the comparison of photoelectron binding energies of Mo(3d) core electrons of different oxidation states as mentioned by several authors. The binding energies of freshly evaporated samples are in good agreement with the values reported for MoO_3 and SiO, respectively, by other workers [4, 5, 10–14].

4. Discussion

It is well known that changes in the valence charge distribution cause the core-level binding energies to shift (chemical shift). In order to interpret the observed XPS results of MoO_3/SiO, it is necessary to

TABLE I Photoelectron binding energies of Mo(3d) and Si(2p) core electrons of amorphous MoO_3/SiO thin films of thickness 300 nm

Film compositions (mol %)	$Mo(3d_{3/2})$ (eV)	$Mo(3d_{5/2})$ (eV)	Si(2p) (eV)
100 MoO_3	235.6	232.6	–
90 MoO_3/10 SiO	235.4	232.3	102.0
80 MoO_3/20 SiO	235.2	232.1	102.1
70 MoO_3/30 SiO	235.0	232.0	102.3
60 MoO_3/40 SiO	234.9	231.9	102.5
50 MoO_3/50 SiO	234.8	231.8	102.6
100 SiO	–	–	101.8

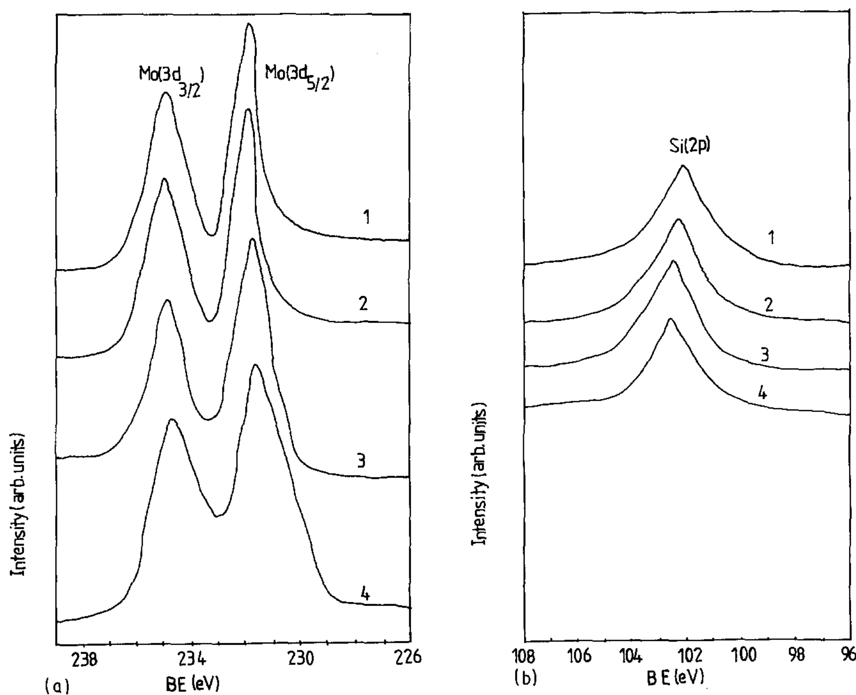

Figure 2 (a) XPS core-level Mo(3d) spectra of MoO_3, and (b) XPS core-level Si(2p) spectra of SiO, for 300 nm thick samples of 70 mol % MoO_3/30 mol % SiO at different substrate temperatures during deposition, (1) 20° C, (2) 100° C, (3) 200° C, (4) 270° C. BE = binding energy.

discuss briefly the crystallographic structure of SiO. The structure of MoO_3 has already been discussed [15]. The structure of SiO_x layers ($0 < x < 2$) as revealed by electron spectroscopy for chemical analysis (ESCA) and confirmed by other workers is strongly dependent on their preparation and existing conditions. SiO is by no means a simple mixture of silicon and SiO_2. Several arrangements different from those associated with silicon and SiO_2 are present. SiO is believed to be composed of clusters of Si–Si and Si–O bonds distributed in such a way as to satisfy the SiO stoichiometry. The random bonding model is based on a statistical distribution of Si–Si and Si–O bonds and can be described by means of substitutional tetrahedra of the type $Si–Si_yO_{4-y}$, ($y = 0, 1, 2, 3$ and 4), which can be strongly distorted. The $Si–SiO_3$, $Si–Si_2O_2$ and $Si–Si_3O$ arrangements are the most likely. In the mixture model [16] there exist only the tetrahedra with $y = 0$ and 4, i.e. a mixture of larger clusters of silicon and SiO_2. In SiO the valence band consists of silicon 3s and 3p orbitals and the conduction band consists of the oxygen 2p orbital.

In the present work appreciable changes in the binding energy of Mo(3d) and Si(2p) line positions are observed with varying composition but the value of the binding energy of the Si(2p) peak for 90 mol % MoO_3/10 mol % SiO is 102.0 eV, which is higher than the binding energy of 100 mol % SiO (101.8 eV). As the content of SiO is increased in MoO_3 the values of the binding energy of Si(2p) line positions are increased. At 50 mol % MoO_3/50 mol % SiO the value of the Si(2p) binding energy is 102.6 eV. The values of Mo(3d) binding energies are decreased by the addition of SiO to MoO_3. The positions of the Mo(3d) and Si(2p) lines are those expected for Mo(V) and SiO_x, respectively. These results can be explained in the following manner. When the molar percentage of SiO is increased in the mixed layers of MoO_3/SiO, there is an increase in overall disorder in the system. Some silicon ions may be incorporated in an MoO_3 lattice which 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) [17, 18]. 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 results in a small increase in the Si(2p) binding energy [14]. The value of binding energy for a pure SiO sample is 101.8 eV and thus is in excellent agreement with the value corresponding to stoichiometric SiO

TABLE II Photoelectron binding energies of Mo(3d) and Si(2p) core electrons for 300 nm thick samples (70 mol % MoO_3/30 mol % SiO) at various substrate temperatures during deposition

Substrate temp. (° C)	$Mo(3d_{3/2})$ (eV)	$Mo(3d_{5/2})$ (eV)	Si(2p) (eV)
20	235.0	232.0	102.3
100	235.0	232.0	102.4
200	234.8	231.8	102.5
270	234.6	231.6	102.6

TABLE III Photoelectron binding energies of Mo(3d) and Si(2p) core electrons for 300 nm thick samples (70 mol % MoO_3/30 mol % SiO) annealed at various temperatures for 2 h

Annealing temp. (° C)	$Mo(3d_{3/2})$ (eV)	$Mo(3d_{5/2})$ (eV)	Si(2p) (eV)
As-evaporated	235.0	232.0	102.3
200	234.9	231.8	102.4
300	234.5	231.4	102.4
400	233.8	230.5	102.5
500	232.6	229.4	102.6

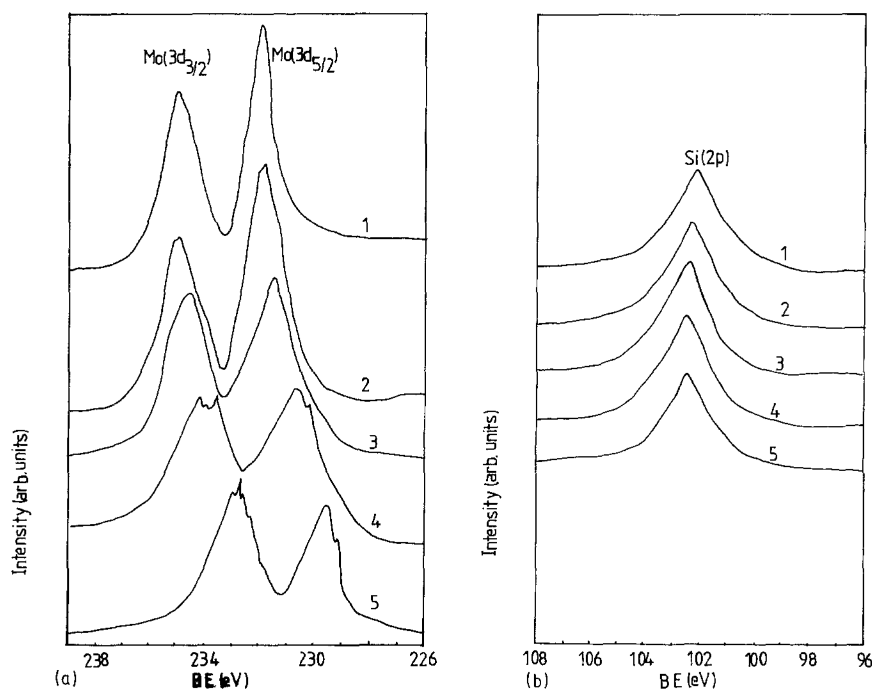

Figure 3 (a) XPS core-level Mo(3d) spectra of MoO_3, and (b) XPS core-level Si(2p) spectra of SiO, for 300 nm thick samples of 70 mol % MoO_3/30 mol % SiO with the substrates at room temperature during deposition, (1) as-evaporated, and annealed at (2) 200° C, (3) 300° C, (4) 400° C, (5) 500° C. BE = binding energy.

[12–14, 18]. A unique SiO species probably does not exist in the solid state. Rather, SiO has the composition $Si\text{-}(O)_x(Si)_y$, where $x + y = 4$ with the most probable composition being $x = y = 2$ [14].

The presence of a single Si(2p) line at 101.8 eV indicates that properly evaporated SiO films are not composed of a simple mixture of silicon and SiO_2. When SiO is mixed in MoO_3 the binding energy is increased from 101.8 to 102.6 eV. This value is in excellent agreement with the value of binding energy assigned to SiO_x, where $x = 1.6$ [17]. Thus the position of the Si(2p) core state shifts monotonically with increasing oxygen concentration from the value of 101.8 to 102.6 eV. SiO_x films have been interpreted in terms of an Si–Si bonding state in the valence band structure of a continuous random network structure in which Si–Si and Si–O bonds are distributed homogeneously. The increase in the binding energy of Si(2p) lines as the content of SiO is increased in MoO_3 is thus due to the change in SiO composition.

The substrate temperature during deposition has a considerable effect on the binding energy of the Mo(3d) doublet but the binding energy of Si(2p) lines is changed slightly. Heating the substrates in vacuum at 200° C or above results in the Mo(3d) doublet appearing at lower binding energies and indicates the formation of a molybdenum species of lower valency. The binding energy of the newly formed molybdenum oxidation state is in excellent agreement with the binding energy assigned to the Mo(V) oxidation state (Table II) [4, 10, 19]. This decrease in binding energy of the Mo(3d) doublet may be due either to the incorporation of silicon ions in an MoO_3 lattice or to the electron transfer from oxygen 2p to the Mo 4d level. The slight change in Si(2p) binding energy due to heating the substrate in vacuum may be due to dissociation of SiO to silicon and oxygen atoms which results in the small increase in Si(2p) binding energy. Heating the substrates does not alter the O:Si ratio but does cause internal chemical changes in the film [14]. Table III shows the XPS core-level Mo(3d) and Si(2p) binding energies of 70 mol % MoO_3/ 30 mol % SiO films annealed at different temperatures in vacuum. After annealing the samples at 500° C the Mo(3d) doublet appears at lower binding energies and indicates the formation of molybdenum species of lower oxidation states. The value of binding energy of the Mo(3d) doublet is in excellent agreement with the binding energy assigned to the Mo(IV) oxidation state [5, 10, 11]. The effect of annealing on the binding energy of Si(2p) lines is not very pronounced. The value of binding energy for the sample annealed at 500° C is the same as was assigned to the sample 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 binding energy for 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 and cause the molybdenum orbital to be a little less tightly bound. This helps the internal electron transfer from an oxygen (2p) to a molybdenum (4d) level due to which molybdenum is readily changed to a lower oxidation state during the heat treatment.

TABLE IV A comparison of photoelectron binding energies of Mo(3d) core level electrons of different oxidation states in thin films of MoO_3/SiO as reported by several authors

Authors	Oxidation state of molybdenum	$Mo(3d_{3/2})$ (eV)	$Mo(3d_{5/2})$ (eV)
Tenret-Neol [10]	6+	235.1	232.0
	4+	231.8	228.6
Jiang Zhi-Cheng [11]	6+	235.5	232.2
	4+	232.2	229.3
Present authors	6+	235.5	232.6
	4+	232.6	229.4

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