

ESR studies of thin amorphous films of MoO₃—effects of substrate temperature, film thickness and annealing procedures

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Electron spin resonance spectra of thin films of amorphous MoO₃ are presented. An increase in spin density associated with increased Mo(V) concentration is found to occur with increased substrate deposition temperature. Plots of spin density against film thickness show a linear relationship, and reveal a significant residual spin density when extrapolated to zero thickness. Resonance signals are observed at $g = 1.92$ and $g = 2.0$ which are attributed to Mo(V) and Mo(III), respectively; that at $g = 1.92$ vanishes on annealing *in vacuo* at 250° C. Colour centres observed at higher substrate temperatures are probably due to the presence of Mo(III).

1. Introduction

Semi-conducting properties of amorphous transition metal oxides have been studied by a number of workers [1, 2]. The origin of the conduction is recognized as an electron transfer or hopping process of unpaired electrons from a transition metal ion in a lower oxidation state to one in a higher oxidation state. Molybdenum (VI) oxide is known to form amorphous semi-conductors with other oxides [2] and electrical conductivity results from electron transfer between Mo(V) and Mo(VI).

Molybdenum (VI) oxide exhibits some interesting physical properties and it is well known that evaporation *in vacuo* or in an inert atmosphere results in the formation of substoichiometric oxides [3]. Many studies of both optical properties and colour centre formation in single crystals as well as in amorphous films have been reported [4–7]. ESR and electrical conductivity measurements have also been reported for single crystals of MoO₃ doped with transition metal ions and for amorphous thin layers [8–11]. The electrical and optical properties of the oxide are extremely dependent upon the stoichiometric balance of the compound and can easily be influenced by the addition of other ions in a variety of oxidation states [4, 8].

In its stoichiometric form, MoO₃ should be a diamagnetic insulator, Mo(VI) having a d⁰ electron configuration. Various processes have been known to produce non-stoichiometry in the oxide resulting in unpaired spins associated with the transition metal (e.g. oxygen deficiency and addition of glass formers, etc.).

The relative proportions of the transition metal ions in different oxidation states has been an important parameter in explaining electronic conduction in oxide films and the technique of ESR with its ability to

detect paramagnetic centres is a powerful tool for investigating the different species present because it can allow estimates of the concentration of the paramagnetic species to be made as well as characterizing the energy states and localization of the unpaired spins.

In many transition metal compounds the unpaired electron is associated with a single atom rather than with many atoms through delocalization processes, and the number per atom and their associated energies will vary both with oxidation state and element. Electron spin resonance has been observed in many studies involving molybdenum oxide [1–9, 12, 13]. Dzhanelidze *et al.* [7] assumed that the centre formed by the trapping of an electron in oxygen vacancies whose level lies close to the top of a conduction band would be spin active, and that it would be possible to detect electron spin resonance in this type of centre. Deb and Chopoorian [3] assumed that the slight increase in ESR signal occurring with increased thickness could be due either to increasing concentration of Mo(V) formed by electron trapping of an Mo(VI) site or to oxygen ion vacancies with Mo(V) as neighbours.

Deb [5] reported the observation of a weak signal at $g = 2.0$ and a strong signal at $g = 1.93$ attributing the former signal to a free electron. Other workers [5, 9, 12, 13] have also observed these two resonances and Ioffe *et al.* [8] reported that ESR studies of the hyperfine structure from Mo(V) in MoO₃ gave information on the state of conduction electrons as well as the kind of compensation of impurities in the crystals.

In addition, some workers [1–9, 12, 13] have studied the ESR properties of MoO₃ under conditions of mixing with other oxides or as single crystals grown under a variety of preparative conditions and it has also been observed that the properties of thin layers vary according to the preparative techniques used.

In this paper we report the studies of the effect of thickness, substrate temperature and annealing temperature upon the ESR properties of thin amorphous films of MoO_3 prepared under high vacuum.

2. Experimental procedure

2.1. Preparation of thin amorphous films

Amorphous thin films of MoO_3 in the thickness range 100 to 600 nm were prepared by evaporation in a Balzers BA510 coating unit on thin fused silica glass substrates. Before preparation these substrate plates were cleaned in solvents, boiling distilled water and finally in a gas discharge plasma at a pressure of 0.1 torr for approximately 20 min. All substrates were held at a temperature of 100°C to improve the degree of adhesion. In studies of the effect of substrate temperature variation, a number of films were prepared at different substrate temperatures by raising the sample temperature to that required (100 to 270°C) using the heater mounted at the inner top of the bell-jar. Films prepared at room temperature showed no evidence of colour but, as the temperature of the substrate was increased, the colour of the film changed first to green and then to blue at higher substrate temperatures.

The oxide was evaporated from molybdenum boats and the evaporation rates and film thicknesses were monitored using an Edwards quartz crystal monitor. Film thicknesses were determined using the technique of multiple beam interferometry [14].

2.2. ESR measurements

The electron spin resonance spectra were recorded using a Varian E3 ESR spectrometer, working at X-band frequency. Constant modulation amplitude, power level, magnetic field scan and recorder settings were used for all samples at present values. The amplifier gain was adjusted for some samples to obtain convenient signal traces. The sample size, determined by the size of the cavity, was a 3 cm length and 1 cm width silica plate fused to two silica rods and adjustment of the position within the cavity was made as for an aqueous cell.

All measurements were made at room temperature. Crystalline copper sulphate was used to estimate spin concentrations. Annealing of samples was studied at temperatures of 200 and 250°C by heating at these temperatures for a period of 2 h.

3. Results

The ESR spectra of layers of amorphous MoO_3 were recorded over the thickness range 100 to 600 nm and in the substrate temperature range 100 to 270°C . Fig. 1 shows ESR spectra for thin layers of amorphous molybdenum (VI) oxide having a fixed composition but of varying thickness. At low intensity, signals were of Gaussian shape changing to Lorentzian as the concentration of the paramagnetic species increased. The variation of the area spin density with film thickness is plotted in Fig. 2. The effect of varying the substrate temperature from 100 to 270°C on films 400 nm thick is shown in Fig. 3 and the intensity of the signal is seen to increase with increasing temperature. Figs 4 and 5 show the linear increase in spin density observed with

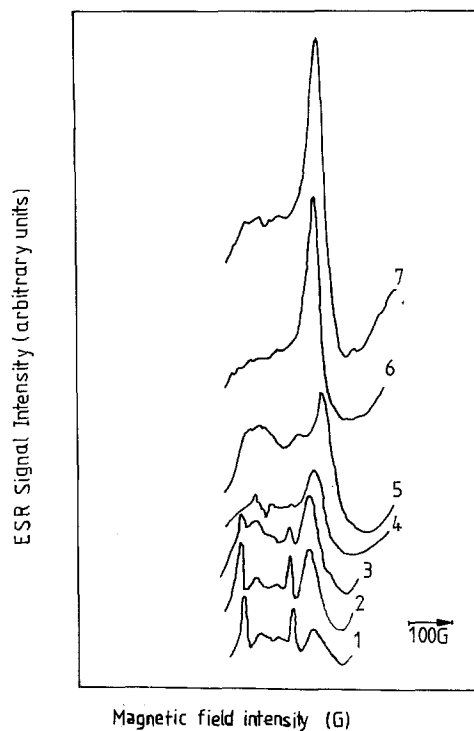


Figure 1 ESR spectra of MoO_3 thin films of thicknesses (1) 100 nm, (2) 200 nm, (3) 260 nm, (4) 300 nm, (5) 400 nm, (6) 450 nm, (7) 600 nm. (Gain 1.25×10^5 .)

increasing film thickness and the increase observed in spin density as the substrate temperature was increased. Annealing studies were undertaken on samples of film thickness 260 and 300 nm by annealing these films *in vacuo* at various temperatures for a period of 2 h, allowing them to cool slowly (rate = 2°C min^{-1}), and when room temperature had been reached, measuring the ESR spectra. Up to 200°C the signal intensity was found to increase, but at 250°C and above the signal at $g = 1.92$ vanished (Fig. 6). A weak signal observed at $g = 2.0$ in all samples was weakened slightly as the thickness increased but was little affected by increased annealing temperature.

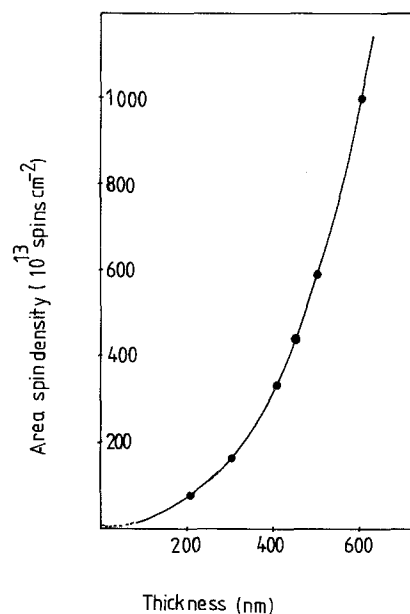


Figure 2 Dependence of area spin density on film thickness for MoO_3 thin films.

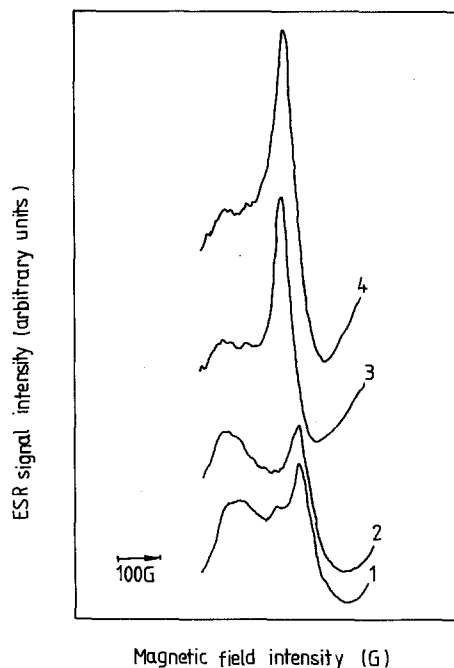


Figure 3 ESR spectra of 400 nm thick films of MoO_3 having substrate temperatures (1) 100°C, (2) 150°C, (3) 200°C, (4) 270°C. (Gain 1.25×10^3 .)

The linear relationship observed in Fig. 2 between area spin density and thickness of the film for samples of fixed composition establishes a bulk property of the material. Extrapolation of this plot to zero thickness leads to a significant residual area spin density of approximately 1×10^{13} spins cm^{-2} .

4. Discussion

Naturally occurring molybdenum is a mixture of isotopes of which 75% have zero nuclear spin (even mass-numbered isotopes) and 25% of which are odd mass-numbered (15% Mo^{95} and 9.6% Mo^{97}). The

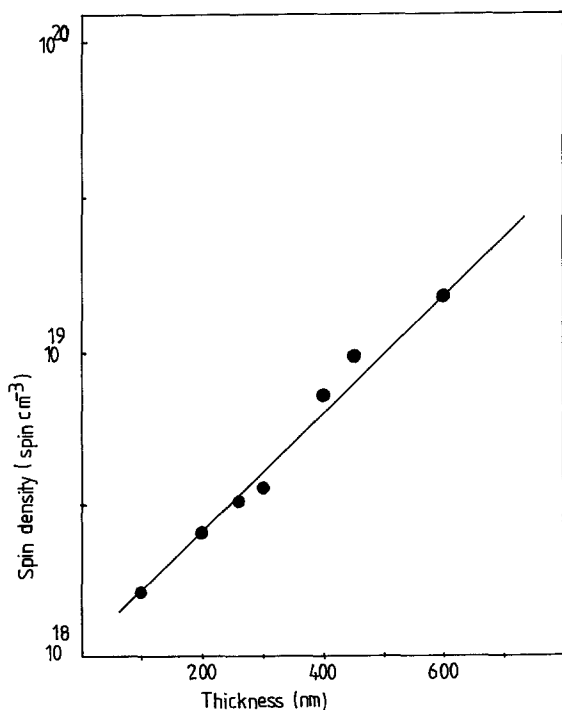


Figure 4 Variation of spin density with thickness of the films of MoO_3 .

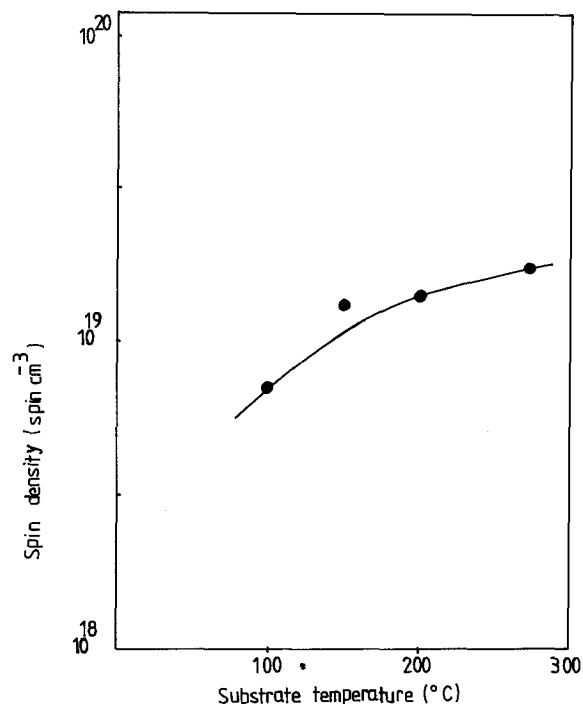


Figure 5 Variation of spin density with substrate temperature of 400 nm thick films of MoO_3 .

expected ESR spectrum is, therefore, a strong single line with six much weaker lines superimposed upon it. The ESR spectra are generally described in terms of an axial spin Hamiltonian.

$$H = \beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A I_z S_z + B (I_x S_x + I_y S_y)$$

where β is the Bohr magneton, S is the electron spin quantum number, g is the Landé splitting factor, I is the nuclear spin quantum number and A and B are parameters. (The three orthogonal directions x , y , z , and the parallel and perpendicular factors are indicated.)

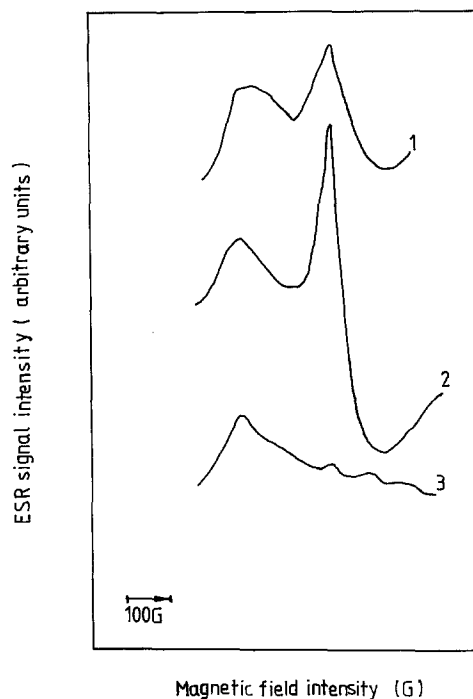


Figure 6 Effect of annealing on 260 nm thick samples: (1) as-evaporated, (2) annealed at 200°C, (3) annealed at 250°C.

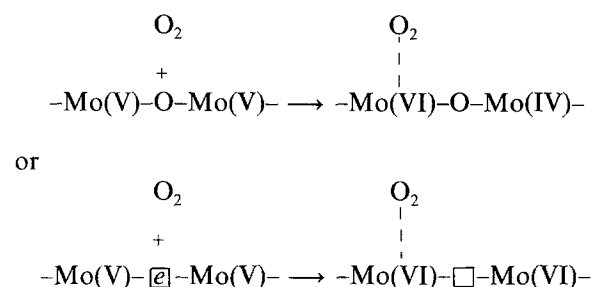
In the case of molybdenum, the oxidation state Mo(VI) is a d^0 species and therefore gives rise to no ESR signal. Of the three common oxidation states, Mo(V), Mo(IV) and Mo(III), the second is a d^2 ion and would not be expected to give rise to a room-temperature signal, leaving the d^1 and d^3 ions, respectively, to be those capable of giving the observed signals. The studies undertaken by previous workers of heat-treated MoO_3 *in vacuo* and under a reducing atmosphere, have indicated the presence of both of these species in the blue, non-stoichiometric oxides, formed during such treatments [9, 15–19] and the spectra obtained by us also indicate the presence of both species – the resonance at $g = 1.92$ being attributed to Mo(V) [3, 8, 9, 12, 13, 17, 19]. A weak signal at $g = 2.0$ has also been observed by other workers and has been variously attributed to the substrate [13], free electrons [5] and Mo(III) [9]. In the present work, the ESR signal at $g = 2.0$ is observed to show a slight decrease in intensity as both the thickness and the concentration of Mo(V) at $g = 1.92$ increases. Annealing was not found to affect the signal at $g = 2.0$ but that at 1.92 could be annealed out completely, suggesting that the weak signal at $g = 2.0$ is due to Mo(III), consistent with the observation of Mann and Khulbe [9].

In order to interpret the observed ESR results it is necessary to discuss briefly the crystallographic structure of MoO_3 . In the crystalline state molybdenum (VI) oxide has a layer structure built up of distorted MoO_6 octahedra. The distortion is caused by off-centre displacement of the metal atoms towards one of the surrounding oxygens. The oxygen atoms are not all equivalent and the Mo–O distances, vary from 0.188 to 0.245 nm with one oxygen in particular being bonded to only one Mo(VI).

In MoO_3 , the valence band consists of oxygen 2p states. The electronic configuration of Mo(VI) is $4d^0$ so the transition of electrons from the valence band 2p oxygen orbitals to the empty Mo(VI) $4d^0$ level gives rise to an incorporation of lower valence state Mo(V) within the lattice.

In the present work the observations may be explained in the following way. The thickness of the samples has a significant effect upon the area density of spins associated with dangling bonds, the latter increasing linearly with increasing thickness of the sample and thus being indicative of a bulk property of the film, i.e. to spins uniformly distributed through the volume of the sample, in agreement with the results of Thomas *et al.* [20] and Sotani [12]. Our value of a residual spin density of approximately 1×10^{13} spins cm^{-2} at zero thickness of the film could be due to spins on the external surfaces. It is well known that MoO_3 loses oxygen on heating *in vacuo* and that thin amorphous layers of molybdenum trioxide contain a number of oxygen vacancies which are positively charged defects capable of capturing one or two electrons. The oxygen vacancies in capturing one or two electrons give rise to singly or doubly charged centres, and an oxygen ion vacancy with a trapped electron is probably associated with an Mo(V) ion. Thus, localization of an electron on a molybdenum (VI) site gives

rise to the formation of an Mo(V) state [9, 10, 16]. One electron of a doubly charged centre may be ionized thermally and give rise to an increase in the number of singly charged oxygen centres and hence to an increase in the concentration of the Mo(V) states as the temperature is raised. Our films which were annealed at a pressure not greater than 10^{-3} torr with a heater wound around a mica frame, may be assumed to incorporate oxygen in the lattice which causes the Mo(V) signal at $g = 1.92$ to vanish (Fig. 6). Because no new signals were observed, we can rule out the formation of any paramagnetic oxygen species such as O_2^- and an explanation similar to the scheme proposed by Sotani [12] of oxygen absorption as an oxygen molecule, and a weak interaction with the Mo(V), probably applies. Thus



Due to annealing, the colour of the samples changes to dark blue and the ESR signal with $g = 2.0$ remains constant which indicates that coloration is most probably due to Mo(III).

Our result is consistent with the results reported by other workers [21, 22], that the signal with $g = 2.0$ was attributed to colour centres. Some other workers [3, 5, 12, 13] reported that both Mo(V) centres and colour centres would be produced simultaneously. Hence it can be said that colour centres are most probably due to Mo(III) and may be due to Mo(V) ions also.

5. Conclusions

Increase in spin density with the thickness in MoO_3 thin amorphous layers is due to increasing concentration of Mo(V) ions. These Mo(V) ions are formed by oxygen ion vacancies in the molybdenum sublattice each with a trapped electron.

When one electron from a doubly-charged oxygen centre is ionized thermally, this increases the number of singly-charged oxygen centres and leads to an increase in the number of Mo(V) ions as the temperature rises. Thus the spin density increases with substrate temperature.

The main ESR signal at $g = 1.92$ is annealed out due to the oxygen incorporation in the film by degassing from the mica sheet during heating at a pressure not higher than 10^{-3} torr. Colour centres are most probably due to Mo(III) ions and may also be due to Mo(V) ions.

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