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Electronic structure of Fe (0–5 at.%) doped MoO₂ thin films studied by resonant photoemission spectroscopy

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Abstract

The electronic structure of pulsed laser-deposited Mo_{1-x}Fe_xO₂ ($x = 0, 0.02$ and 0.05) thin films has been investigated using resonant photoemission spectroscopy near the Mo 4p absorption edge. In all the samples a broad Fano-like resonance peak at ~ 46 eV is observed in the whole area of the valence band, which indicates the contribution of the Mo 4d states in the entire valence band region. The doping of Fe in these films leads to a decrease in Mo 4d states contributing to electronic states at lower binding energy region. In addition to this, we also observe a shoulder at 4.9 eV in the valence band spectra of doped samples. It is proposed that the origin of this shoulder is due to the Fe hybridized states.

1. Introduction

The transition metal oxides exhibit a variety of interesting physical properties [1]. One particular interesting phenomena is that these oxides show a wide range of electrical conductivity, which varies from insulator (e.g. NiO, TiO₂, MoO₃) to semiconductor (e.g. NbO₂) to conductor (e.g. WO₂, MoO₂). Among these compounds molybdenum oxide shows variable electrical conductivity from the metallic MoO₂ to insulating MoO₃ phase with variation in oxygen content [2, 3]. Recently molybdenum oxide has attracted much interest because of its unique properties and applications in gas sensing devices [4, 5], optically switchable coatings [6], catalysis [7], etc. In MoO₂, another degree of dimensionality in terms of its magnetic property may be induced by doping some magnetic impurity. The resulting device material will be the new dilute magnetic oxide for present MoO₂-based technologies. In our recent paper [8] we reported the room temperature ferromagnetism in (100) oriented Fe-doped molybdenum oxide thin films grown on a *c*-axis sapphire substrate using pulsed laser deposition. The x-ray photoelectron spectroscopy revealed that Fe is in the +2 state, which favours the substitutional occupancy of Fe ions in the MoO₂ matrix.

From the fundamental physics point of view as well as to find out the origin of ferromagnetism in iron-doped samples, it is essential to have a knowledge of the electronic structure of both undoped and doped samples, particularly around the Fermi level. The electronic structure of MoO₂ has been investigated theoretically by means of a phenomenological molecular orbital scheme as well as by tight-binding and cluster calculations [9–12]. Experimentally it is shown by various spectroscopic measurements that the 9 eV wide occupied band can be divided into two energy regions, 3 eV wide Mo 4d bands at low binding energy region and 6 eV wide O 2p bands at higher binding energies [2, 10, 12–15]. Resonant photoemission spectroscopy (RPES) is a well-known technique for obtaining detailed information on the valence electronic structure of a material [16–19]. To the best of our knowledge, there is hardly any report available on RPES measurements on doped or undoped MoO₂ in the existing literature. In the present paper, we report our results of resonance photoemission measurements on pulsed laser-deposited Fe (0–5 at.%) doped MoO₂ thin films. The energy of the incident photon is varied around the Mo 4p \rightarrow 4d threshold. The contribution of Mo 4d states to the various regions of the valence band and the effect of Fe doping are discussed on the basis of the analysis of the resonant behaviour of the valence band emission.

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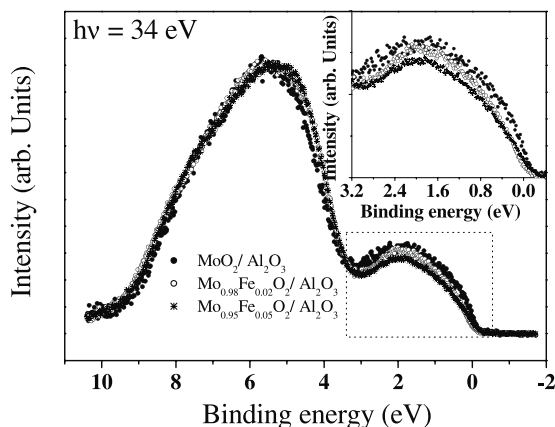


Figure 1. Valence band spectra recorded at 34 eV photon energy of undoped and Fe-doped $\text{MoO}_2/\text{Al}_2\text{O}_3$ thin films grown by the pulsed laser-deposition technique. The inset shows the expanded view of the lower binding energy region.

2. Experimental details

Thin films of undoped and Fe (2 and 5 at.%) doped MoO_2 were grown on *c*-plane sapphire single-crystal substrates by the pulsed laser ablation technique as discussed in [8]. X-ray diffraction (XRD) revealed that all the samples are in single phase. The homogeneity of the samples was checked with the energy-dispersive analysis of x-rays (EDAX) technique. The thicknesses of all the films are around 200 nm as measured by a stylus profilometer. The x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), resistivity and magnetization measurements were performed for the characterization of these samples. These results are reported elsewhere [8]. The RPES measurements on these samples were carried out at the angle-integrated PES beamline on the Indus-1 synchrotron radiation source. The valence band photoemission spectra were recorded using a photon energy of 34–68 eV in steps of 2 eV. All the spectra were measured using an Omicron (EA125) energy analyser. The angle between incoming photon and emitting electron was 90° , while the angle between sample and photon beam was 45° . The acceptance angle of the spectrometer was $\pm 8^\circ$ during the measurements. All measurements were carried out at room temperature. The spectra were normalized by the photon flux estimated from the photocurrent from the post mirror of the beam line. The background pressure in the analysis chamber was 1×10^{-10} mbar. The sample surface was cleaned using 1 keV Ar ions. Before performing RPES measurements the surface composition was estimated from core level XPS measurements. The Fermi level was aligned by recording the valence band spectra of the *in situ* cleaned Au foil. The total experimental resolution was estimated from the Fermi edge of the gold foil. The experimental resolution, dependent on the photon energy, was estimated to 0.32–0.44 eV in the photon energy range 34–68 eV.

3. Results and discussion

Figure 1 shows the valence band (VB) spectra of undoped and Fe (2 and 5 at.%) doped MoO_2 thin films, recorded

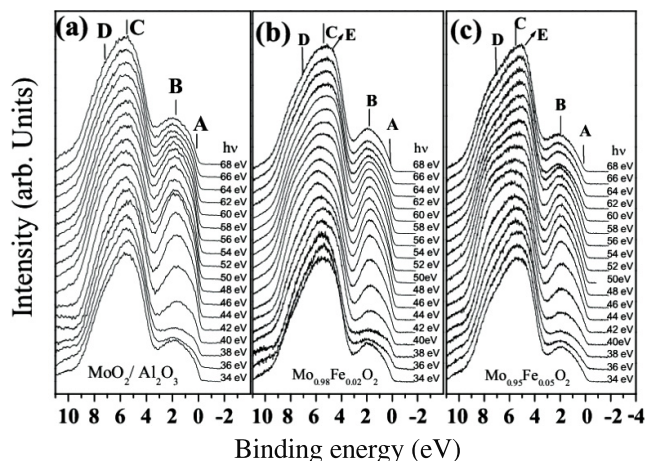


Figure 2. Valence band spectra of (a) $\text{MoO}_2/\text{Al}_2\text{O}_3$, (b) $\text{Mo}_{0.98}\text{Fe}_{0.02}\text{O}_2/\text{Al}_2\text{O}_3$ and (c) $\text{Mo}_{0.95}\text{Fe}_{0.05}\text{O}_2/\text{Al}_2\text{O}_3$ as a function of photon energy from 34 to 68 eV. All spectra are normalized to the intensity of the mainly O 2p derived feature C.

with 34 eV photon energy. The background obtained by the Shirley procedure [20] has been subtracted from each raw data. All the spectra show a finite density of states at the Fermi level, indicating the metallic nature, in confirmation with the resistivity measurements [8] of these films. The width of the VB spectra is close to the reported theoretical and experimental results [12, 13]. The VB spectra corresponding to all three films consist of two dominant bands and a hump; the lower binding energy band peaked at 1.8 eV and the higher binding energy band peaked at 5.5 eV and the hump is at 6–8 eV. These spectra match well with the reported spectra of MoO_2 (bulk) [10, 13]. Comparison of the observed spectra with those of the theoretically calculated density of states (DOS) [11, 12] indicates that the lower binding energy band is mainly derived from Mo 4d states while the higher energy band is mostly derived from the O 2p states. A hump at 6–8 eV is derived from hybridization of the O 2p and Mo 4d states. On comparing the valence band spectra of the undoped and Fe-doped samples a small shoulder at 4.9 eV binding energy was observed. Normally Fe 3d states are observed around 1–3 eV, but since the 0–3 eV region is dominated by Mo 4d states and Fe concentration is very small, therefore, these states are not visible in the valence band spectra. In order to understand the electronic structure of MoO_2 thin films and the effect of Fe doping in detail we have carried out RPES measurements on both undoped and doped MoO_2 films by varying the incident photon energy in the Mo 4p \rightarrow 4d absorption region.

Figures 2(a)–(c) show valence band spectra of undoped, 2% Fe-doped and 5% Fe-doped MoO_2 thin films taken at various photon energies, respectively. In order to further analyse the data we divide the valence band spectra into four regions namely (i) near the Fermi edge (0.15 eV)—feature A, (ii) the peak region of lower binding energy band (1.8 eV)—feature B, (iii) the peak region of higher binding energy band (5.5 eV)—feature C and (iv) the hump region (7.1 eV)—feature D. Each spectrum in figure 2 is normalized by the peak intensity of feature C. We have normalized the spectra with the intensity of feature C because this feature is mainly

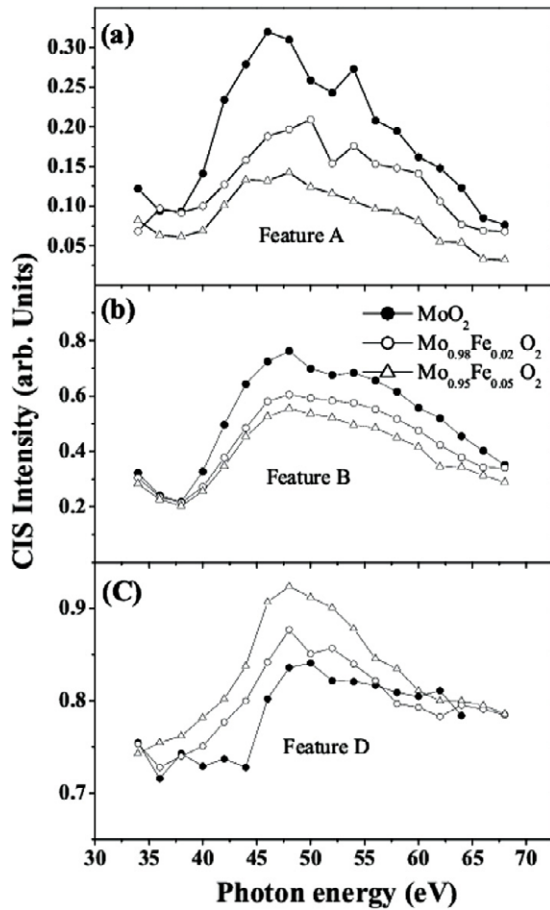


Figure 3. CIS photoemission intensities of (a) feature A (at binding energy 0.15 eV), (b) feature B (at binding energy 1.8 eV) and (c) feature D (at binding energy 7.1 eV) as a function of photon energy for MoO₂/Al₂O₃, Mo_{0.98}Fe_{0.02}O₂/Al₂O₃ and Mo_{0.95}Fe_{0.05}O₂/Al₂O₃, respectively.

due to O 2p derived states and resonance is recorded at the Mo 4p → 4d absorption edge. Further, the photoemission cross section for the O 2p state does not change appreciably over such a narrow energy range [21]. Thus it is expected that the intensity of feature C would not change significantly. It is evident from the figure, when the photon energy is varied from 34 to 38 eV, a marginal decrease in the intensity of features A, B and D is noticeable. The intensity of these features increases monotonically for photon energies between 42 and 48 eV. The intensity of these features again decreases with further increase in photon energy. Further, increase in the intensity of features A and B is much more significant in comparison to the increase in the intensity of feature D. Similar variations in the VB spectra with photon energy have been observed in all the 2% and 5% Fe-doped MoO₂ films (figures 2(b) and (c)).

To evaluate the resonance energy and effect of iron doping we have plotted constant initial state (CIS) intensity plots for features A, B and D for all the three films in figure 3. The CIS intensity plots shown in figure 3 and 4 are obtained from figure 2 by plotting the normalized intensity of the marked regions (A, B and D) at fixed binding energy positions of the respective features. A maximum in the intensity of these spectra around a photon energy of 46 eV

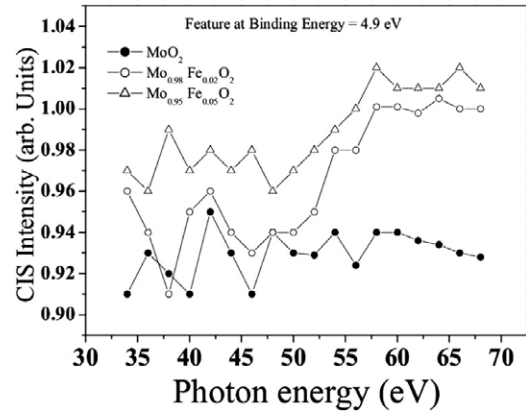


Figure 4. CIS photoemission intensities of feature E (at binding energy 4.9 eV) as a function of photon energy for MoO₂/Al₂O₃, Mo_{0.98}Fe_{0.02}O₂/Al₂O₃ and Mo_{0.95}Fe_{0.05}O₂/Al₂O₃, respectively.

is observed for features A, B and D. This resonance energy matches with the previously reported resonance value for the Mo 4p → 4d absorption region for Mo₂C single crystal [22–24]. The observed $h\nu$ dependence is characteristic of the Fano lineshape [25], and the maximum of the photoemission intensity is interpreted as originating from the interference between the normal Mo 4d photoemission process and the process induced by the photon-induced excitation, $Mo\ 4p^6 4d^n + h\nu \rightarrow Mo\ 4p^5 4d^{n+1}$, followed by the emission of a Mo 4d electron through a super-Coster-Kronig decay, $Mo\ 4p^5 4d^{n+1} \rightarrow Mo\ 4p^6 4d^{n-1} + e^-$. In a similar resonant photoemission study of α -Mo₂C (0001) performed by Sugihara *et al* [23], they found a resonance peak at 46 eV due to Mo 4p → 4d transition and observed the contribution of the Mo 4d orbital included in the whole area of the valence band region. In another study Lince *et al* [26] performed a resonant photoemission study for MoS₂ and found that the Mo 4d derived non-bonding band showed a resonance due to the Mo 4p → 4d transition at ~42 eV. Our results are in agreement with these studies [22–24].

The energy dependence of feature A is shown in figure 3(a) for all three samples. For Fe-doped samples the behaviour of feature A is similar to the undoped MoO₂ film showing resonance at 46 eV. Moreover, with the increase in Fe content a decrease in the intensity of feature A is evident from the figure. Variation in the intensity of feature B with photon energy is shown in figure 3(b) for all samples. The resonance effect here is also similar to that of feature A. As in the case of feature A, in feature B a decrease in the intensity is also observed with Fe doping while the overall behaviour of the feature with photon energy remains the same. In figure 3(c) we show the variation in intensity of feature D with incident photon energy. Feature D also has a resonance peak at ~46 eV, similar to features A and B but the resonance effect is weaker in comparison to the one observed for features A and B. Moreover, in contrast to the behaviour of the intensity of features A and B, it can be noted here that the intensity of feature D increases with Fe doping.

From the above observations it is evident that all three features A, B and D in the MoO₂ exhibit resonance around

46 eV. The resonance is stronger for features A and B in comparison to feature D. This is in agreement with the earlier reported band structure calculations according to which features A and B are mainly due to Mo 4d states while both Mo and O 2p hybridized states contribute to feature D. When Fe is doped into MoO₂ films, the effect of doping is clearly reflected in these CIS spectra. With the increase in Fe content the resonance effect for features A and B weakens while for feature D an enhancement in the resonance effect is observed. This would indicate depletion in the Mo 4d states' contribution to features A and B. These states are possibly partly replaced by Fe 3d states, which may be the reason for the increase in the conductivity and observation of ferromagnetism in the doped films. The increase in intensity of feature D with Fe doping suggests an enhanced hybridization of Mo 4d and O 2p states. In our XPS study on these films [8] it is observed that, after Fe doping, the Mo⁴⁺ contribution increases. Since the ionic radius of Mo⁴⁺ is larger than Mo⁵⁺ or Mo⁶⁺, we may expect an enhanced hybridization. However, to further verify this claim, theoretical band structure calculations on Fe-doped MoO₂ are needed.

To understand the origin of the shoulder at 4.9 eV (feature E in figures 2(b) and (c)), we have plotted CIS intensity at binding energy 4.9 eV versus the incident photon energy for all the samples (figure 4). These CIS intensity plots show an increase in the intensity at around 56 eV for Fe-doped samples, which happens to be the Fe resonance energy (Fe3p → 3d absorption region). This resonance is absent in the undoped MoO₂ films. These observations suggest that the feature at 4.9 eV is an indication of Fe in the hybridized state. Though, in the present work we have studied the effect of Fe doping in the electronic structure by resonant photoemission spectroscopy, to have an insight into the origin of ferromagnetism in the Fe-doped samples, a technique like spin-resolved photoelectron spectroscopy would be more useful.

4. Conclusions

In conclusion we have studied the electronic structure of pulsed laser-deposited Fe (0–5 at.%) doped MoO₂ thin films using resonance photoemission spectroscopy. The observed VB spectra are similar to those observed for bulk MoO₂. The observation of a finite density of states at the Fermi level of these VB spectra indicates the metallic nature of the films. The Fe doping in the MoO₂ up to 5 at.% does not have much influence on the valence band spectra of these films but shows a small reduction of Mo states at the lower binding energy region. When the photon energy is varied from 34 to 68 eV, in the Mo 4p → 4d transition threshold region, the resonance is observed at photon energy 46 eV for all the films. We have also observed a shoulder in VB spectra of doped samples at

binding energy 4.9 eV, which is attributed to the Fe hybridized state.

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